SURFACE REACTIONS IN THE INTERSTAGE ANNEALING OF
PHOSPHATED MILD STEEL

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ABSTRACT

An introductory section describes the cold extrusion process. A works investigation into a cracking problem is then described which indicated that the cracking is associated with the formation of an abnormal coating during the re-phosphating cycle after interstage annealing. When the steel was normalised in a reducing atmosphere, if the initial layer of phosphate and lubricant was incorrectly removed, part of the coating reacted to produce a diffused metal layer containing a dispersed non-metallic phase.

Tests showed that zinc was largely volatilised and played no significant part in the reaction. Phosphorus, in the form of an iron phosphate coating and of phosphorus pentoxide, was found to produce the layer under investigation. Sodium salts as an additive to phosphate coatings promoted the reaction by retaining larger quantities of phosphoric oxide as a stable slag. Carbon as an additive produced no significant effect.

Moisture in the hydrogen atmosphere increased the concentration of inclusions in the surface layer. These contained a high concentration of manganese and there was an
impoverishment of manganese in the surrounding areas.

Pickling experiments showed that the phosphorus rich layer destroyed the immunity to acid attack conferred by the inhibitor used. The layer was found to produce a reduction in surface ductility with fine cross-cracking similar to that seen in extruded cups.

Annealing in a vacuum reduced severity of the attack, but did not eliminate it completely. By using a cyanide solution for cleaning before annealing, the phosphate-soap coating could be removed much more effectively than with the normal caustic soda solution, and the resulting reaction suppressed.

It was concluded that the best method of control is by an improved preliminary cleaning cycle using a cyanide solution.
ACKNOWLEDGEMENTS

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1. **INTRODUCTION**

The investigations described here began with the examination of persistent cracking in a typical extruded steel component and this led to a study of the effects of traces of residual lubricant on the components during interstage heat treatment and the reaction of these coatings with the steel surface.

1.1. **Nomenclature**

For the sake of brevity the term 'annealing' is used here to indicate high temperature softening processes in general. Where a particular process is intended the terms 'sub-critical annealing', 'full annealing' or 'normalising' are used.

In subsequent sections a sample sawn or cropped from bar will be known as a blank; a partially extruded preform as a slug; the term lubrication will refer to the complete phosphate plus soap treatment, and re-lubrication to the same sequence carried out after partial extrusion and annealing.

1.2. **Development of the cold extrusion process for steel**

The application of cold extrusion to steel commenced in Germany and much of the subsequent development was carried out there and in the United States; Feldmann (1) and Wick (2) give brief historical details. The cold extrusion process
had been used since about 1886 for soft metals and the process was later extended to alpha brass by L.E. Hooker in 1909 and became widely used in the small arms industry.

The first experiments on the cold extrusion of steel were made in 1934 at the Kabel and Metallwerken Neumeyer A.G. in Nuremberg. In 1935, A. Liebergeld succeeded in extruding a steel case from a cold mild steel cup, using a press tool designed for deep drawing brass cartridge cases (3). The case was cracked and heavily scored and it was evident that the friction arising from the high deformation pressures required an intermediate lubricating layer. The solution to this problem was at hand in the work by Dr. Singer who, in 1934, had filed a patent on the use of surface coatings such as metallic oxides or salts for the cold working of iron and steel and phosphate or oxalate coatings were recommended (19).

In the United States, war-time experiments led to the development of a production process for the manufacture of artillery shell cases (6, 7, 8) and in the last decade the process has been used for a number of civil applications and several papers have been published giving process details (9, 10, 11).
After the war, the process was examined in this country, at the Royal Ordnance Factory, Birtley, as a method for manufacturing artillery shell cases (12). It has since been adopted by a number of companies for the manufacture of small parts, and research into the principles of the cold extrusion process is being carried out at the National Engineering Laboratory, East Kilbride (34) and at the Production Engineering Research Association (32).

1.3. Present Position of the Cold Extrusion Process for Steel

The cold extrusion of steel is now employed as a method of mass producing small parts, and the technology of the process is governed very largely by the need to minimise production costs, (12).

The process will produce components of a high accuracy and surface finish requiring little finish-machining and strengthened by mechanical work but, on the other hand, the stresses on the tools are high, and the capital and tooling costs are also very high.

1.4. Materials

The extrusion pressure required for a steel is proportional to the carbon content and to the annealed
hardness of the material (1), and although a number of applications of the process to higher carbon and even alloy steels have been described (2) the only steel to which the full range of extrusion techniques have been applied is low carbon mild steel with a maximum carbon content of 0.15%, fully killed for uniformity of properties.

1.5. Lubrication

A successful lubricant must be able to withstand extreme pressures up to 140 t.s.i., the rubbing action as the workpiece flows over the tool and the consequent increase of surface area, without permitting metal to metal contact. In addition the lubricant must not build up as a permanent deposit on the surface of the tools.

The lubrication problem was solved originally by applying a phosphate coating and by using this as a carrier for a lubricant soap. It has since been shown that other solid lubricants can be used (14, 15), but that none of these coatings is as satisfactory as the original (13, 25) and, as far as is known, all plants operating on an industrial scale, use the phosphate-soap system of lubrication. The techniques used at the present time for producing the phosphate coating have been described in a number of publications, (16, 17, 18).
These are based on the deposition of a fairly heavy coating of zinc phosphate which is then treated with a sodium stearate lubricant.

The solution used for phosphating contains zinc phosphate \((\text{Zn}(\text{H}_2\text{PO}_4)_2)\) in dilute phosphoric acid, the concentration of ingredients and the temperature being so balanced that they are just held in solution. Zinc phosphate exhibits an inverse solubility/temperature relationship and maintaining the bath at \(95^\circ C\) assists the formation of insoluble phosphates \((38)\). According to Machu \((20)\), the excess acid reacts with the steel to form the soluble primary iron phosphate, liberating hydrogen and causing the pH of the solution to rise at the interface:

\[
\text{Fe} + 2\text{H}_2\text{PO}_4 = \text{Fe}(\text{H}_2\text{PO}_4)_2 + \text{H}_2 \quad (1)
\]

The solution is unbalanced, hydrolysis of the metastable phosphates occurs and they crystallise out in a sparingly soluble secondary form.

\[
\text{Zn}(\text{H}_2\text{PO}_4)_2 = \text{ZnHPO}_4 + \text{H}_3\text{PO}_4 \quad (2)
\]

\[
\text{Fe}(\text{H}_2\text{PO}_4)_2 = \text{FeHPO}_4 + \text{H}_3\text{PO}_4 \quad (3)
\]

The hydrolysis proceeds a stage further to yield the insoluble tertiary phosphate.

\[
3\text{ZnHPO}_4 = \text{Zn}_2(\text{PO}_4)_2 + \text{H}_3\text{PO}_4 \quad (4)
\]

\[
3\text{FeHPO}_4 = \text{Fe}_3(\text{PO}_4)_2 + \text{H}_3\text{PO}_4 \quad (5)
\]

Strict attention to solution composition is required to
confine this precipitation to the metal surface (21). Midgley (22), referring to solution of iron and manganese phosphates, postulates that the initial attack by free acid on the metal surface is an electrolytic process and that phosphate crystals are first found on pearlite grains.

Other ions which are present in proprietary phosphate solutions include nitrite, which oxidises the excess iron formed during reaction (1) to an insoluble sludge which is removed periodically.

\[ 2\text{Fe(H}_2\text{PO}_4\text{)}_2 + O = 2\text{FePO}_4 + 2\text{H}_2\text{PO}_4 + \text{H}_2\text{O} \]  

\[ \text{(6)} \]

The nitrite also acts as a depolarising agent by combining with the hydrogen formed in reaction (1). Other substances which may be added to modify the grain size and deposition rate of the coating include compounds of nickel and 'condensed' phosphates containing the \((\text{NaPO}_3)_6\) ion. The coating produced is generally believed to contain phosphates of both zinc and iron, although James (19) has stated that by suitable control of the conditions all the dissolved ferrous iron can be kept in solution. Doss (23) however has shown that the proportions of zinc, iron and
phosphate remain approximately the same within wide limits and the ratio is not affected by the accelerators used. These approximate proportions are stated to be 32.3% Zn, 12.3% Fe and 40.8% P0₄ with the remainder assumed to be water. The coating is crystalline and isomorphous with minerals of the type M₃(P0₄)₂₄H₂O (31, 36, 38). The coating weight obtained varies between 30 and 450 mg/dm² corresponding to a thickness of between 1 and 15 microns (1).

A number of soaps, fats and oils are employed as lubricants in conjunction with the phosphate layer (1, 13, 18, 19, 33). The most important are sodium fatty acid soaps, exemplified by sodium stearate, which are the easiest to apply commercially. Phosphated components are immersed in an aqueous solution of the soap and this is followed by draining and drying. The final coating consists of three layers:

(a) a water soluble layer;
(b) a water insoluble, alcohol soluble layer;
(c) the phosphate layer.

The water soluble layer is evidently the sodium soap. The intermediate layer is formed by a reaction between the phosphate and soap layers and is probably a zinc soap. The
reaction may be promoted when the lubricating solution has a pH in the range of 8.5 - 9.0. The commercial lubricants may also contain small quantities of buffer chemicals, to maintain the correct alkalinity, and rust inhibitors.

The coefficient of friction at high unit pressures of samples lubricated with sodium stearate compares favourably with samples treated with other lubricants (19, 25).

In practice, the complete phosphating and lubricating sequences also include a preliminary degreasing and pickling operation and a number of intermediate rinses and conditioning dips. An example of a complete commercial sequence is given later (Table 1).

1.6. Interstage Annealing

The more complex shapes are produced in a series of operations with interstage annealing followed by rephosphating and lubricating between extrusion. The cheapest annealing treatment is a re-crystallisation below the lower critical temperature and this is adequate for most of the low carbon steels employed. Temperatures recommended vary between 620°C and 700°C (1), (12).
However, the degree of deformation imposed on the workpiece is not uniform and Okell has noted (24):

"It is not unknown to discover that a certain location in an extruded part has developed abnormally large grains. The phenomenon ---- is the familiar critical strain grain growth ----. They can be so large that etched surfaces display grains readily discernible to the naked eye. Further working of such a structure is not easy as rupture readily, and the surface of a strained large-grained specimen has the characteristic rough 'orange peel' appearance. A finished component with such grains is correspondingly weak, especially when subjected to shock loading".

The critical strain grain growth is very common in preformed blanks which have been subcritically annealed, because the average degree of deformation is low. The difficulties in subsequent working are most pronounced when the subsequent series of forming operations includes a draw. An example of grain growth in a subcritically annealed preformed slug is shown in Fig.1.

When exaggerated grain growth must be avoided, a normalising process can be employed. Normalising at the
usual temperature of 950°C for low carbon steels results in a workpiece needing a higher extrusion pressure than one sub-critically annealed. However, Tilsley and Howard have shown that a higher normalising temperature of 1050°C for 0.1% carbon steel reduces this extrusion pressure appreciably (32). The higher normalising temperature results in a somewhat larger, although uniform, grain size and this is believed to be responsible for the lower extrusion pressure.

Tests carried out in the author's works tend to confirm that higher normalising temperatures give lower extrusion pressures (Table 2). For both subcritical annealing and full normalising treatments, a slow rate of cooling is desirable to reduce the elements dissolved in the ferrite to a minimum (24), if minimum punch pressures are required.

The importance of the surface condition of the workpiece has already been emphasised in Section 1.5 and, on the Continent, the recommended practice is to use a protective atmosphere for subcritical annealing (1). This is not essential however, and the relatively thin scale formed at this temperature can be removed by pickling before the subsequent phosphating operation (11). If a normalising treatment is employed the use of a protective atmosphere is however essential as the metal loss on pickling would otherwise be too great.
1.7. The effect of annealing on lubricant coatings

A survey of the literature on phosphating and extrusion revealed little previous work on the effect of annealing on phosphate coating. Feldmann (1) stated "Before bright annealing workpieces they should be cleaned and degreased. This can be done in a special plant. Alternatively, it may be done as part of the annealing process in an oxidising atmosphere in the first chamber of the furnace. When degreasing by combustion in this way care should be taken to prevent chemical reaction between the lubricant and the surface of the steel". He did not specify the measures to be taken to prevent this reaction.

James (29) stated that the phosphate coating dehydrates at about 150°C but phosphate is still present in a modified form at 500°C. Subcritical annealing was said to produce a completely dehydrated phosphate, partly modified to pyrophosphate. The coating was said to become volatile at about 950°C and normalising above this temperature to result in complete removal of the phosphate coating. If soap is present in addition to phosphate, this was said to burn off satisfactorily if the atmosphere is oxidising, but reducing atmospheres may produce a scale and burnt-in lubricant film which is rather difficult to pickle. Apart from increased pickling time James did not anticipate any further difficulties.
Cupr (30) studied the decomposition of zinc phosphate coatings on steel surfaces by X-ray and thermo-gravimetric analysis and reported that dehydration occurs in two stages: at temperatures above 210°C the tetrahydrate \((\text{Zn}_3\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}\) is converted to dihydrate and above 400°C anhydrous zinc phosphate is formed. At 850°C the phosphate decomposes into a reddish brown crystalline mass which no longer appears to be a phosphate. This new phase was not identified.
2. THE CRACKING OF EXTRUDED CUPS

The researches, which are the main subject of this thesis, were prompted by a works investigation into cracking difficulties experienced during the manufacture of a particular extrusion and in order to explain the problem a summary of this preliminary investigation is given here.

2.1. Description of Component

The sequence used to produce the component is illustrated in figure 2.

The material used is a mild steel, fully killed with silicon, of the following nominal composition:

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>S</th>
<th>P</th>
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<tbody>
<tr>
<td>0.15%</td>
<td>0.10/0.35%</td>
<td>0.50%</td>
<td>0.05%</td>
<td>0.05%</td>
</tr>
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max. max. max. max. max.

The blanks are phosphated and stearate coated after Stage 1 and the preformed slugs are annealed, and relubricated after stage 2. The complete sequence of lubrication is given in Table 1.

An interstage annealing operation is required after the preforming operation in order to put the material into a satisfactory condition for backward extrusion. To avoid
difficulties with critical grain growth, which is not obliterated near the rim of the cup, a normalising operation is carried out in a reducing atmosphere of partly burned towns gas. A temperature of 1050°C was chosen to reduce the punch pressure as much as possible (14).

2.2. Form of Cracking

During the backward extrusion operation, defective components were produced, the defect taking the form of a circumferential crack on the inside wall of the cup, close to the junction between wall and base. The cracking occurred intermittently and was more obvious in some batches of slugs than in others. A typical crack is shown in Fig.3.

2.3. Details of Examination Procedure

2.3.1. Physical

Thirty six cups were produced by the sequence 1 - 3 in figure 2 in three separate batches, and each was subjected to a detailed examination as follows:

(i) The base thickness and external height were measured.
(ii) The severity of cracking was measured as the angular length of crack or cracks.

(iii) The coating weight was determined by chemically stripping the phosphate and stearate and re-weighing. It was expressed with reference to the original area of the slug as mg/dm².

(iv) The final weight of the cup was recorded as the slug weight.

(v) Hardness tests were made at the rim of the cup where deformation was least.

The Data have been tabulated (Table 3). The various parameters plotted against severity of cracking and the correlation coefficients, as determined by the Bravais-Pearson ranking method (26), are given in Figs. 4 - 8. The regression equations were determined by the method of least squares (27) and the regression lines are drawn in the appropriate figures.
The results suggested an inverse relationship between cracking severity and base thickness (Fig. 4), an inverse relationship between cracking severity and slug weight (Fig. 5), and a direct relationship between coating weight and cracking severity (Fig. 6). The samples fell into two distinct groups, the first consisting of parts of normal weight and coating weight and the second of light components of abnormally high coating weight (Fig. 8).

A visual examination of the bore of the extruded cups revealed that in addition to the major crack near the base, the inner surface of the defective cups was covered with fine cracks, running at right angles to the direction of extrusion while the surface of the satisfactory cups was free from this effect. The difference between the bore surface of good and bad components is shown in Figs. 9 and 10.

2.3.2. Metallographic examination of cracked cups

Metallographic examination threw some light on the mechanism of metal flow in the unsatisfactory extrusions. In the initial stages the metal flowed smoothly round the base of the punch and up the wall, but at a later stage a resistance to metal flow at the extreme surface led to
discontinuities in the flow lines as the flow changed
direction to maintain the continuity of the extrusion.
As the disturbance to the grain flow became more severe
small cracks began to form (Fig. 13). Finally, when the
base thickness of the cup had been reduced beyond a certain
level, the major crack developed along one of the parallel
planes of cross deformation, as shown in Fig. 14.

2.4. Examination of preformed slugs

Preformed slugs from satisfactory and unsatisfactory
batches were examined before extrusion. Hardness test
results on the surface and on a cross-section of the slugs
before extrusion were similar (Table 4). The grain size
and metallographic structure of both batches was the same.
There was however a great difference in slug weight and
coating weight between the two samples, and the surface
appearance of the two samples after removing the phosphate/
lubricant coating was markedly different, the sample from
batch 1 being rough and pitted while that from batch 2
was smooth. The difference between the two surfaces is
illustrated in Figs. 11 and 12.
2.5. Discussion of Results

2.5.1. General Considerations

The development of cracks indicated that tensile or shear forces were generated in the abnormally coated slugs. Evidently the surface layer ceased to flow but the material in the interior continued to flow around the dead metal leading to a change in direction of the grain flow. As the resistance to flow around the stationary metal increased, due to work hardening, the forces rose to a value sufficient to start the stationary metal moving again for a period. These unstable conditions led to the formation of a series of fine cross cracks on the inner surface of the extrusion and the main crack developed subsequently.

2.5.2. Results - Summary and Conclusions

One of the factors involved was evidently the base thickness of the cup and a number of authorities have discussed the optimum ratio of base to wall thickness (2, 12, 14, 28).

From the data in Table 3, it was evident that another factor besides base thickness was involved, that the unsatisfactory components were underweight and had a high phosphate/lubricant coating weight on rephosphating, and that the unsatisfactory slugs were badly pitted. All
three observations may be explained by excessive attack by sulphuric acid at the pickling stage prior to repolphating the annealed slug; the inhibitor failing to protect the metal. An excessive build-up of iron-rich sludge in the pickling bath was discovered on subsequent investigation and this confirmed that heavy attack had taken place.

A slight increase in the original weight of the cropped blank produced a thicker base and so reduced the frequency of cracking to an acceptable level, but the real solution lay in preventing excessive attack during pickling and it was decided to study the factors involved in the annealing process.
3. **Preliminary Investigation into Factors Affecting the Annealing Process**

3.1. Preliminary Considerations

At the author's plant, the procedure for stripping the slugs before annealing consisted of immersion for 10 minutes in warm alkaline cleaner. This was believed to remove the lubricant soap layer but to do no more than loosen the phosphate coating.

It was decided to investigate the effect of completely stripping the coating, of removing the soap only, and of leaving the composite coating intact, followed by normalising in a reducing atmosphere.

3.2. Experimental Procedure

3.2.1. Material

The material used was 1\(\frac{1}{2}\)" dia. black bar to B.S.970EN2E specification. Chemical analysis was as follows:

- C: .10%
- Si: .14%
- Mn: .44%
- S: .030%
- P: .022%
- Ni: .20%
- Cr: .069%
- Cu: .28%
The blanks were lubricated and preformed to slugs. Alcohol soluble soap and total coating weights were determined by the method given in 3.2.2. and found to be within the normal range. The results were: soap 100 - 210, phosphate 154 - 354 and total 337 - 455 mg/dm$^2$.

### 3.2.2. Determination of Coating Weights

The following procedure was adopted for the determination of the lubricant coating weight:

1. The surface area of the sample was calculated from measurements, as $A$.

2. Samples were weighed to give $W_1$.

3. Alcohol soluble soap was removed by boiling for 10 minutes in methyl alcohol.

4. Samples were blown dry and re-weighed to give $W_2$.

5. Phosphate coating was removed by boiling in 20% NaOH solution for 20 minutes followed by scrubbing under hot running water.

6. Samples were rinsed with methyl alcohol, blown dry and reweighed to give $W_3$. 
(7) Coating weight of soap was calculated as
\[
\frac{W_1 - W_2}{A}
\]
Coating weight of phosphate was calculated as
\[
\frac{W_2 - W_3}{A}
\]
Total coating weight was calculated as
\[
\frac{W_1 - W_3}{A}
\]
All coating weights were expressed in mg/dm².

3.2.3. Conditions Investigated

The following methods of stripping the old coating were investigated:

(1) Coating completely stripped with NaOH, as described in section 3.2.2. (5).

(2) Coating partially removed by the standard production method of immersing in warm alkaline cleaner for 10 minutes at 150°F (65°C).

(3) Soap only removed with methyl alcohol, as described in section 3.2.2. (3).

(4) Coating not removed.
The samples were normalised at 950°C or 1130°C for 20 minutes in a reducing atmosphere and cooled in the atmosphere (partly burned towns gas). They were then pickled in 5 litre beakers in a laboratory pilot plant under the conditions given in Table 1 (operations 1 - 4).

All test pieces were weighed before and after each stage and examined optically and metallographically. A summary of the treatments is given in Table 5.

3.3. Results of Examination

The weight changes after stripping, after annealing and after pickling are given in Table 6, and shown graphically in Fig. 15, where the weights and weight changes are expressed as a proportion of the original weight. (The coating weight determined for each batch was used as the reference weight for that batch). The figures compared are the averages for the batches examined.

Slugs which were completely stripped changed very little in weight during annealing and lost only a negligible amount in pickling, (Fig. 15.1). The slugs had a clean matt surface after each treatment. Fig. 19 shows the surface appearance of a sawn slug after stripping, annealing and pickling. Microsections showed no appreciable change in the surface of the slugs.
Slugs which were not stripped lost an average of 75% of the total coating weight during annealing (Fig. 15.4). The slugs had a bright, silvery surface after normalising. The undersides showed scars in the bright surface due to reaction with the wire mesh belt of the furnace (Fig. 16). On many of the slugs the surface was blistered in the side and upper surfaces (Fig. 17) having apparently been molten at some stage in the reaction. Microsections through the slugs after normalising showed an apparently porous surface layer which appeared to be continuous in crystal structure with the base material (Fig. 18).

During pickling, the slugs annealed without stripping suffered a very heavy weight loss, equal to 700 to 800% of the coating weight (Fig. 15.4). Visual examination showed that the slugs were heavily pitted and covered with black smut. The contaminated material from the reaction with the wire mesh belt was not attacked and stood proud of the heavily pitted surface (Fig. 20). Fig. 21 shows a section through the heavily pitted surface after pickling and part of a wire scar, which is seen to be a separate phase from the ferrite matrix.
The slugs which were partially stripped either in alcohol or in alkaline cleaner lost 25% of the total coating weight in stripping and a further 35% on annealing (Fig. 15.3). Visual examination showed a bright surface layer with slight wire scars. Metallographic examination showed that the unsound surface layer was present although the layer was shallower than that on the slugs which were not stripped at all. On pickling, there was a weight loss averaging 120% of the original coating weight (Fig. 15.2).

An attempt was made to eliminate the reaction between the mesh belt of the conveyor furnace and the slugs which had not been stripped by normalising them at 1130°C on a mild steel tray. Partial welding between slug and tray took place and this led to very heavy weight losses.

3.4. Discussion of Results

The results of the tests carried out, indicated that both phosphate and soap-phosphate coatings are not completely volatilised when heated in a reducing atmosphere at temperatures between 950 and 1130°C, but that a part of the coating reacts with the steel surface to form an alloy layer.
4. PRELIMINARY LABORATORY TESTS

4.1. Considerations

Before proceeding with the main investigation it was thought desirable to check that the coatings produced in the laboratory gave the same effect as those produced in the works, and that the reaction between freshly prepared coatings and metal during annealing would be similar to that found with partially extruded samples. Extrusion might affect the situation, firstly because the temperature may rise momentarily as high as 1000°C at the surface (30), and secondly because some lubricant may be transferred to the tools.

4.2. Experiments

4.2.1. Experimental Procedure

Eighteen sample blanks cropped from 0.954" dia, bar taken from the sample batch reserved for the experiments (Section 5.4), were pickled, phosphated and lubricated in a laboratory pilot plant (Table 1).

The blanks were divided into three groups which were treated as follows:

(a) Not deformed
(b) Lightly deformed to produce a 'preformed' slug
(c) Heavily deformed to produce a cup with an extrusion ratio of 72%.
Two samples from each batch were partially stripped to remove the soap coating, two were completely stripped and two were left with the coating intact. The weight of the coatings was determined.

A summary of the different treatments given to the samples before normalising is given in Table 7.

All the samples were then annealed for 20 minutes at 950°C in partially burned town gas and cooled in the atmosphere. The weight change on heat treatment was measured, and one sample from each pair was sectioned for metallographic examination.

The remaining samples were then degreased (Table 1 operations 1 - 4), dried and reweighed. All samples were then examined visually using a low power binocular microscope, and sectioned for microscopical examination.
4.2.2. Results of Examination

The changes in weight recorded at different stages are shown in Table 8. There was an appreciable variation in the initial coating weight, which masked any variation during the deformation stage. The completely stripped samples suffered small weight losses on annealing and on pickling. All degrees of deformation gave broadly similar results.

Samples from which the soap coating had been removed lost between 19 and 26 mg. in weight during the annealing operation, but this still left between 22 and 30% of the original coating absorbed into the steel surface. On pickling the weight losses exceeded those of the completely stripped samples by a factor of 10, the degree of deformation making very little difference.

The results on the samples annealed with their coatings intact are very similar to those of the partly stripped samples. Taking the last two sets of results together, there is a slight tendency for the undeformed coatings to give higher weight losses on pickling but the differences are too small to be considered significant.
On visual examination, the completely stripped samples had a bright matt finish after annealing, and a grey matt surface after pickling, while the coated samples had an unnaturally bright finish after annealing, and a black smutty finish after pickling. On the heavily deformed specimens this effect was most pronounced on the upper rim and outside diameter of the cup and absent on the base and inside diameter.

Metallographic examination of the samples after annealing showed all specimens to be decarburised to a depth of 0.1 - 0.2 mm. Samples which had the phosphate-soap coating intact showed a relatively sound surface layer, but beneath this a subsurface layer of non-metallic material (Fig. 23). Samples from which the soap layer had been removed before annealing did not have a metal layer at the surface, but did have the non-metallic layer (Fig. 24). Fig. 24 also shows a considerable penetration of the non-metallic material parallel with the grain flow.

The maximum depth of the non-metallic layer was .02 mm on the O.D. and .05 mm on the sheared faces of the undeformed and lightly deformed samples. The heavily deformed samples showed similar effects but
the distribution was uneven. On the base of the cup, the maximum depth of the non-metallic layer was .02 mm while on the rim and in isolated areas on the O.D., the depth of penetration was as high as .07 mm.

Figs. 23 and 24 show the samples etched very lightly in 1% nital, to preserve the non-metallic phase. When the samples were etched in Stead's reagent or heavily etched in nital a diffused metal surface layer was revealed .07 - .08 mm deep. It was found that these heavier etching techniques tended to dissolve the non-metallic phase, leaving a series of holes.

4.2.3. Discussion of Results

It was considered that the weight loss in heat treatment of the completely stripped samples might be due to decarburisation. The surface area of the undeformed test pieces was 21.6 cm² and assuming 0.1% carbon was lost from the surface to a depth of 0.1 mm, calculation indicates that this would represent a weight loss of 1.68 mg per specimen.
The weight losses of 5 to 7.5 mg recorded on completely stripped samples are thus of the right order of magnitude, for this mechanism to afford a possible explanation.

The uneven distribution of penetration on the extruded cups normalised with the phosphate or phosphate-soap coating in position was thought to be due to the redistribution of the phosphate/lubricant coating which is known to occur on extrusion. Some figures were available from another investigation (35) to show the variation in coating weight from place to place on an extruded cup, and so the depth of penetration on sample C6 and C2 was measured in corresponding positions and the two distributions compared, as in Table 9. Each of the depths of penetration recorded is the mean of three determinations taken at random positions within the area designated, and represents the maximum depth of penetration of the non-metallic constituent.

The correlation between the depth of penetration, and the coating thickness is indicated in Fig. 25.
The conclusions which may be drawn from this investigation are as follows:

(a) Reactions between lubricant coatings and steel surfaces on heating in a reducing atmosphere are similar on undeformed and deformed specimens. In the case of severely deformed specimens the distribution of the coatings and of the reaction product becomes uneven.

(b) The unsound layer observed in the earlier investigation is evidently a non-metallic phase dispersed in the metallic matrix.

(c) The maximum depth of penetration of the non-metallic phase appears to be related to the concentration of the coating on the surface, other factors being constant.

(d) The laboratory lubricant coating reacted similarly to the production coating, indicating that no unknown factors were present in the original tests.

4.3. Consideration of the thickness of a reduced phosphate coating

Two explanations of the metallographic evidence were considered. First, that the coatings were reduced
by the furnace atmosphere to liberate the metals present as iron or as an iron-zinc alloy at the surface. Once a continuous film has been reduced, the rate of the reaction would decrease and part of the coating could remain as isolated unreduced particles. The alternative hypothesis was that the layer observed was the result of diffusion into the surface of the steel specimens. In order to indicate the relative likelihood of these two explanations a calculation of the approximate film thickness which would result from reducing the phosphate coating to metal in the absence of diffusion into the steel specimen was made and compared with the thickness of the surface layers observed in the experiments. For the purpose of these calculations the chemical mechanism of the supposed reduction was not considered.

These calculations were based on results obtained in the previous experiment (Table 8), and are given below:

<table>
<thead>
<tr>
<th>Average results for sample groups</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total coating wt. gm.</td>
<td>0.0539</td>
<td>0.0583</td>
</tr>
<tr>
<td>soap wt. gm.</td>
<td>0.0192</td>
<td>0.0159</td>
</tr>
<tr>
<td>Phosphate wt. gm</td>
<td>0.0347</td>
<td>0.0424</td>
</tr>
<tr>
<td>Surface area cm²</td>
<td>21.6</td>
<td>22.3</td>
</tr>
<tr>
<td>Phosphate coating wt mg/dm²</td>
<td>161</td>
<td>192</td>
</tr>
</tbody>
</table>
**Thickness of Phosphate layer**

The approximate analysis of the phosphate layer is Zn 30%; Fe 10%; P_4O_10 40%; H_2O 20%. We may assume that the coating is:-

- **75% Zinc orthophosphate (\(\kappa\)-Hopeite):**
  \[ \text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} \quad \text{S.G.} = 3.04 \]

- **25% Ferrous orthophosphate (Vivianite):**
  \[ \text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} \quad \text{S.G.} = 2.58 \]

and that the specific gravity of the coating is the weighted mean, 2.925. The approximate coating thickness is as follows:-

<table>
<thead>
<tr>
<th></th>
<th>Phosphate wt. gm.</th>
<th>Phosphate volume, c.c.</th>
<th>Surface area cm^2</th>
<th>Layer thickness mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0347</td>
<td>0.0119</td>
<td>21.6</td>
<td>0.0055</td>
</tr>
<tr>
<td></td>
<td>0.0424</td>
<td>0.0145</td>
<td></td>
<td>0.0065</td>
</tr>
</tbody>
</table>

**Thickness of iron layer**

If it is assumed that the whole of the coating were volatilised with the exception of the 10% iron which remains as a metal film, taking the density of iron as 7.9 gm/cc, the approximate film thickness would be as follows:-
Phosphate wt. gm. | 0.0347 | 0.0424
Iron wt. gm. | 0.00347 | 0.00424
Iron volume c.c. | 0.000439 | 0.000537
Surface area cm$^2$ | 21.6 | 22.3
Iron layer thickness mm | 0.0020 | 0.0024

Thickness of iron-zinc layer

If it is assumed that the iron and zinc remain unvolatilised to form an alloy containing 75% zinc, 25% iron and the density is the weighted mean of the densities of iron and zinc (7.33 gm/cc), the approximate film thickness would be as follows:

| Phosphate wt. gm. | 0.0347 | 0.0424
| Iron wt. gm. | 0.00347 | 0.00424
| Zinc wt. gm. | 0.01041 | 0.01272
| Iron-zinc wt. gm. | 0.01388 | 0.01696
| Iron zinc volume c.c. | 0.00189 | 0.00232
| Surface area cm$^2$ | 21.6 | 22.3
| Iron zinc layer thickness mm | 0.00088 | 0.00104

Thickness of layers observed experimentally

Observed thickness of
metallic layer mm | 0.07 - 0.08 | 0.07 - 0.08
max. depth of non-metallic layer mm | 0.02 - 0.05 | 0.02 - 0.05
Although the calculations contain a number of assumptions which reduce their accuracy it is evident that the observed thicknesses are very much greater than could be accounted for by a reduction of the phosphate coating, and the observed layers must be the result mainly of diffusion into the surface of the steel samples.

4.4. A Consideration of the Diffusing Elements

It is reasonable to assume that we are dealing with a diffusion process, preceded by chemical reactions involving the phosphate and soap.

The qualitative analysis of the phosphate coating is well known (19, 23, 31, 36, 37, 38, 39), and it is clear that we have to consider zinc, iron, phosphorus, oxygen, hydrogen from the phosphate coating and sodium and a \( \text{C}_{17} \text{H}_{35} \text{COO} \) radical from the soap coating. The latter will either evaporate or decompose on heating and can contribute only carbon. Hydrogen and carbon could act as reducing agents but not produce the observed phenomena directly. Iron can also be eliminated. Oxygen could have played some part in the formation of the subsurface non-metallic phase. (40, 41, 42, 43).
The elements sodium, zinc and phosphorus were thought worthy of special study. There are theoretical reasons for believing that sodium will not alloy directly with iron, and recent studies suggest that, apart from decarburisation, there is no reaction between sodium and carbon steels at temperatures well above 800°C \((40, 44)\). Differences in atomic diameter also indicate that solid solutions of sodium in zinc are not likely. Sodium can however act as an oxygen barrier to cause corrosion of iron \((46)\).

Zinc is soluble in iron forming an extensive series of solid solutions. The iron rich end of the iron-zinc equilibrium diagram above 782°C consists of austenite, containing zinc in solid solution in equilibrium with the liquid or vapour phase. The maximum solubility of zinc in austenite varies from about 35% at 850°C to about 25% at 1130°C. At room temperature, ferrite contains not more than about 8% Zn under equilibrium conditions, and at higher concentrations a second phase will be present. The boiling point of zinc is 907°C.
There is an extensive literature on the reaction of zinc with steel surfaces (47 - 54). All of these investigations have, however, been carried out at temperatures much lower than those of interest in this investigation. At the highest temperature investigated, 750°C, iron was found to have a greater affinity for phosphorus than zinc (49).

Phosphorus will alloy with iron and has a limited solid solubility in ferrite. At room temperature, the maximum solubility in ferrite is about 1%. At higher concentrations, a second phase is present. At temperatures above 1050°C, if the concentration exceeds 2.8%, a liquid phase is present which solidifies as the phosphide eutectic. Phosphorus will diffuse in solid iron but the atomic size ratio is less favourable than for zinc and the rate of diffusion is generally slower. The diffusion of phosphorus in iron has been investigated over a wide temperature range (55, 56, 57, 58).
5. **EXPERIMENTAL TECHNIQUES**

5.1. **Laboratory Furnace Equipment**

The equipment used for heat treatment is shown in Fig. 30° and, diagrammatically, in Fig. 26. The furnace was of \(2^{1/2}\) KW rating and could be run at temperatures up to 1150°C. Two retorts, constructed in Nimonic 75 material, of internal dimensions \(\frac{3}{4}\)" diameter x 18" deep terminated in a water cooled steel flange with 'O' ring seals onto which the retort heads were clamped. These contained the atmosphere connections and an air admittance for vacuum treatments.

The gas flows were measured by flow meters, and controlled by needle valves after pressure reduction to a suitable level. The moisture content of the atmosphere could be increased by passing it through a wash bottle containing a sintered glass diffusion plate to disperse the gas. The moisture content could also be reduced to a very low level by passing the gas through a proprietary dryer (Birlec 'Lectro dryer') in which the moisture was absorbed by activated alumina.
A small number of annealing treatments under high vacuum were carried out in an 18" modular vacuum unit supplied by Torvac Limited capable of an ultimate vacuum of $10^{-6}$ Torr (Fig. 31).

5.2. **Furnace Atmospheres**

In the preliminary tests the normalising treatments were carried out in a production furnace with partially burned town gas, a complex mixture of $N_2$, $H_2$, $CO$, $CO_2$ and $H_2O$. It was found that coated samples annealed in hydrogen produced an identical reaction product to that found in the earlier tests. Subsequently, all treatments in a reducing atmosphere were carried out in commercial purity bottled hydrogen, whose moisture content was varied to control the oxidation potential. Commercial purity nitrogen was used for purging and backfilling.

A few treatments were carried out in air, and for this compressed air at 80 p.s.i. was passed through oil and water traps, and reduced in pressure before being metered into the retort.
The retort and gas line could be evacuated by a three stage oil filled rotary mechanical pump, either for purging or for vacuum treatments. A McLeod Gauge was used for measuring pressures in the range $10^{-1} - 10^{-3}$ torr. The highest vacuum obtainable in the retort was found to be 0.05 torr but with coated test pieces present, a practicable working pressure was 0.1 torr.

A Foster Recording Controller was used to control the furnace temperature, and the results of temperature surveys and heating rate determinations within the retort at 650, 950 and 1050°C are given in figs. 27 and 28. The thermocouple was inserted in a drilled test piece (fig. 27 inset) within a standard load of six test pieces. The tests indicated that there was a zone 6" long within which the temperature did not vary by more than 5°C and subsequently test loads were loaded so that samples were located within this zone. All test pieces were suspended from the top of the retort with soft iron wire so that they did not come into contact with the sides of the retort.
Details of the standard purging cycle and the gas flows and pressures are given in Table 10.

5.3. Dimensions and Surface Finish of Test Pieces

Four types of test piece were used in the investigation. Most of the tests were carried out using blanks (Fig. 29a) machined from bar. The two parallel faces were ground and an identification number was stamped in the centre of one face.

Two series of tensile tests were carried out. In the first, standard 0.564" diameter tensile test pieces were employed (Fig. 29b). In the second, the surface area to volume ratio was increased by using a flat test piece (Fig. 29c) cut from bright rolled sheet, using a template, and polished to a 000 emery finish. A special test piece for testing the effect of chemicals in powder form was also cut from sheet (Fig. 29d).

5.4. Materials

The type (a) blanks were machined from the same batch of 0.953" dia. hot rolled black bar to specification BS 970 En2E. A qualitative spectrographic examination was carried out followed by a confirmatory wet analysis. The results are given in Table 11 (a).
Standard tensile test specimens were cut from 1\(\frac{1}{2}\)" diameter bar from the same cast of steel, the analysis of which is given in Table 11 (b).

Flat tensile test pieces were cut from bright rolled strip to BS.970 En2E specification, and the results of the analysis are given in Table 11 (c). The material was normalised in an inert atmosphere in order to bring it to the same condition as the bar material before used.

5.5. Surface Treatments

The experimental surface treatments were carried out in 5 litre glass beakers, fitted into protective steel drums. The solutions were heated where necessary with thermostatically controlled immersion heaters.

The following surface treatments were investigated:

(a) The Bonderite 181X phosphating process, using the proprietary chemicals supplied by Pyrene Limited.

(b) Phosphating with a pure zinc phosphate solution prepared from zinc and orthophosphoric acid.

(c) Phosphating with an orthophosphoric acid solution to produce an iron phosphate coating, free from zinc (39).
(d) Zinc plating from a cyanide bath.

The following substances were used to represent the soap coatings:

(a) Commercial Bonderlube supplied by Pyrene Limited (Sodium Stearate).
(b) Stearic Acid.
(c) Graphite.
(d) Sodium Carbonate.
(e) Sodium Hydroxide.

In addition, some tests were carried out using:

(a) Phosphoric Oxide.
(b) Phosphoric oxide and sodium phosphate in powder form.

The specifications and principal impurity limits of the chemicals used are shown in Table 12.

5.5.1. Bonderising

The Bonderite 18IX phosphating procedure is as shown in Table 1.

Regular coating weight determinations indicated that a uniform coating weight of 180 mg/dm² was being obtained (Table 14). Samples of the coating were removed and
analysed using the methods described by Bush, Higgs and Box (63). Results are given in Table 14.

5.5.2. Zinc Phosphate Treatment

The phosphating solution was prepared by digesting 100 gm. of zinc powder with 180 ml of phosphoric acid solution and 100 ml water in a reflux condenser to produce the following reaction:

\[ \text{Zn} + 2\text{H}_3\text{PO}_4 = \text{ZnH}_2(\text{PO}_4)_2 + 2\text{H}_2 \]

the quantities being adjusted to leave a small excess of zinc at equilibrium.

The reaction commenced in the cold and external heat was applied gradually as the reaction subsided, until a temperature of 70°C was reached. The solution was digested at 70°C for 2 hours, boiled until precipitation of phosphate commenced. After diluting to 800 ml, the pH was adjusted to 4.5 with orthophosphoric acid. The phosphating sequence is given in Table 13 (a). The coating weights and analysis of the coating obtained are given in Table 14.

5.5.3. Phosphoric Acid Treatment

Preliminary tests were carried out using a 4M solution of orthophosphoric acid at 70°C as recommended by Donovan, Scott and Shrier (39), but this resulted in a
light coating weight. It was found that by increasing the temperature of the bath to 90°C a heavier coating was obtained. Details of the original and the modified treatments are given in Table 13 (b), and the results of tests on the coating are given in Table 14.

5.5.4. Zinc Plating

The zinc plating was carried out in a bright zinc cyanide plating solution and the conditions adjusted to produce a coating thickness of .0005". Details of the treatment sequence and plating conditions are given in Table 13 (c).

5.5.5. Stearates, Graphite and Sodium Salts

The commercial Bonderlube lubricant was made up to a strength of 7% w/v, pH adjusted to 8.5 with NaOH and applied as shown in Table 1, sections 8 - 11. Coating weights are given in Table 14.

Stearic acid was applied by heating the acid to 90°C, dipping the test pieces and draining off the excess. The weight increase is given in Table 14.
Graphite was applied as a suspension in white spirit. Samples were dipped and dried at 70°C for 10 minutes. The weight increase after drying is given in Table 14. The appearance after drying indicated good uniformity and coverage.

Sodium carbonate was applied as a thin paste into which the specimens were dipped individually. The specimens were then dried for 2 hours at 110°C. The gain in weight was reasonably uniform (Table 14).

Sodium hydroxide was made up as a 20% w/v solution with water into which the specimens were dipped. Although this was in many ways the most satisfactory sodium salt, it softened the underlying phosphate layer and decreased its adhesion. To prevent any loss of coating, samples were loaded into the furnace immediately after the treatment and no separate drying operation was attempted. Special care was taken when loading the wet samples into the furnace to hang them in such a way that they could not touch or drip onto one another. It is considered that the moisture would have been driven off during the initial stages of heating. Samples for
measurements of coating weight were withdrawn from the retort after 20 minutes heating in air, cooled and weighed. There was no evidence of any mechanical loss of coating on these specimens. Coating weight measurements are given in Table 14.

5.5.6. Additional Tests

Tests were carried out to compare the effects of phosphoric oxide and mixtures of phosphoric oxide and sodium phosphate. The test piece is shown in Fig. 29d.

To prevent excessive pickup of moisture from the atmosphere by the phosphoric oxide between packing and heating, the surface of the specimen was covered with transparent adhesive tape after packing the cavities. This was found to be satisfactory and a blank run indicated that the residual ash did not affect the reaction of phosphoric oxide with the steel. It was found that mixing the phosphoric oxide with the hydrated sodium phosphate produced a reaction product which was partially liquid at room temperature.
Attempts at preliminary dehydration of the salt were not successful and the two substances were therefore weighed and added separately to the test plate and allowed to react before covering with the adhesive film.

The test plates were supported in the retort by wires from the four corners so that the test surface was horizontal.

5.6. Heat Treatments

Samples were heated at temperatures of 650°C, 960°C and 1050°C, holding for 2 hours at 650°C and normally for 20 minutes at the higher temperatures, in air, dry hydrogen, wet hydrogen, low vacuum and high vacuum. The combinations of surface treatment and furnace condition investigated are summarised in Table 15.
5.7. Stripping Treatments

For removing the phosphate coating prior to heat treatment, the normal alkali cleaning method was represented by a 10 minute immersion in 20\% w/v NaOH solution at 70°C. Comparative tests were made with a 10 minute immersion in 7.5\% w/v NaCN and 15\% w/v NaOH at room temperature as suggested by Eisler (62).

5.8. Pickling Treatments

Pickling was carried out with a 10\% v/v, sulphuric acid solution made up with 0.1\% of a proprietary inhibitor and artificially aged with an addition of 1\% w/v ferrous sulphate as recommended by Jackson, Steadman and Riley (60). The solution was renewed frequently to maintain the iron content at about the same level to produce a more uniform of attack.

5.9. Weight Changes

Samples were weighed on a direct reading analytical balance, sensitivity 0.0001 gm, capacity 200 gm. The blanks weighed approximately 60 gm with a surface area of 0.22 dm².
Samples were weighed before and after coating with lubricants to determine the quantity of lubricant applied. This method could not be adopted for phosphate coating however, as there is a net loss in weight and extra samples were used for coating weight determinations (3.2.2.).

Specimens were weighed before and after annealing and pickling.

5.10. **Surface Examination**

Samples were examined with a binocular microscope under oblique illumination. Photographs were taken on a Vickers projection microscope using a 100 mm camera lens without eyepiece and oblique illumination at a magnification of X 2½ diameters.

5.11. **Metallographic Procedures**

Sections were cut from the type (a) test pieces normal to the outside diameter and to the parallel faces. The sections were mounted and polished using a diamond polishing system to avoid rounding the edges.
Etching was carried out with a 3% nitric acid in alcohol solution or with Stead's reagent made up as follows:

1 gm. Cupric Chloride and 4 gm. Magnesium Chloride were dissolved in a small quantity of hot water and then diluted with 1 ml. Conc. HCl, 20 ml water and 100 ml ethyl alcohol, in that order.

Specimens were immersed for about 1 minute, repeated if necessary to obtain a suitable contrast.

Measurements were made of the depth of the diffused metallic layer, of the maximum depth of non-metallic inclusions and of the depth of pitting where appropriate using a bench microscope fitted with a graticule eyepiece. All measurements recorded were the mean of nine readings taken in random positions.

All microphotographs were taken at a magnification of X300 diameter on the Vickers projection microscope.
5.13. Mechanical Tests

Tensile tests were carried out on a Denison Universal testing machine of 15 tons capacity. The following properties were determined: upper and lower yield points, maximum stress and load at fracture (from observations of the dynamometer), elongation and reduction of area (from the test piece). The load at fracture and the reduction of area were used to calculate the true U.T.S. on the reduced section.

After testing, the samples were subjected to a careful surface examination under the binocular microscope.

5.14. Analytical Procedures

Phosphate samples were obtained by scraping a freshly deposited sample, using a Beryllium copper tool to avoid contaminating the deposit with iron. Weighed samples were dissolved in dilute nitric acid and then analysed using the methods described by Bush, Higgs and Box (61) for the principal constituents (Table 14).
Samples of the diffused metal layers were obtained by turning off shallow surface layers from a number of specimens and analysed for zinc and phosphorus by standard wet methods of analysis. Other test pieces were examined qualitatively with a Bausch and Lomb dual grating spectrograph to determine if there were any unsuspected elements in the coated sample. This was followed by a detailed quantitative comparison of the zinc lines (Table 29).

Samples were examined by X-ray crystallographic and scintillation techniques (Table 29). A number of residues prepared by igniting phosphate and lubricant coatings were also examined by X-ray crystallography. The results of these examinations are summarised in Fig. 79.

A sample was examined by the Cambridge X-ray scanning micro-analyser at the Cambridge Instrument Company. The sample was a mounted micro-specimen reduced in size to a 1 cm. cube including 1 specimen edge supported by mounting plastic. The distribution of iron, manganese, zinc and phosphorus was examined by photographing and slow line scans (Figs. 39, 44, 80, 81 and 82).
5.15. **Miscellaneous Tests**

Samples of zinc phosphate, zinc phosphate/sodium stearate and sodium stearate coatings were ignited in air and in hydrogen at 650°C, 950°C and 1050°C. The samples were ignited in fire clay boats in a horizontal tube furnace. The residues were examined visually and submitted for X-ray diffraction and chemical analysis (Fig. 79).

A particle of the glassy slag phase detached from a phosphated and annealed sample (P 102), was supported on platinum wire, and heated at successively higher temperatures and examined under the binocular microscope for signs of melting. The results of these tests indicated a melting range of 800 - 1200°C.

5.16. **Test Results**

Experimental conditions for all the tests carried out are given in Table 15, and results for each test series in Tables 16 - 25. In subsequent sections each of the relevant factors will be discussed in turn and reference made to the appropriate tables. The tables of metallographic results record the depth of
pitting, depth of diffused layer, maximum depth of non-metallic inclusions, and depth of decarburisation. The gravimetric and visual tables include the weight losses on annealing and pickling, the visual appearance after annealing and pickling and the depth of pitting after pickling.
6. THE INFLUENCE OF MINOR CONSTITUENTS AND ADDITIVES IN THE COMMERCIAL COATING

6.1. Procedure

In order to determine the effect of addition agents and impurities in the commercial coating, two series of tests were carried out.

In Series E1 specimens coated with Bonderite 181X were compared with specimens coated with pure iron phosphate (deposited from phosphoric acid), with and without a top coat of Bonderlube 235, when annealed at 950°C in hydrogen and air (Tables 15).

Type (a) blanks were coated, annealed and pickled. The progress of the tests was followed gravimetrically, visually and metallographically.

The results were not conclusive as the coating of iron phosphate produced with the original conditions (Table 14) was too thin. The tests were repeated in series E5, with a heavier iron phosphate coating, and the Bonderite 181X and iron phosphate were each coated with either Bonderlube 235 or sodium hydroxide. The tests were carried out at 1050°C in dry and wet hydrogen (Table 15).
6.2. Results

Table 16 gives the metallographic results obtained in series E 1 and Table 20 those for series E 5. Tables 17 and 21 give the results of visual and gravimetric examinations from experiments E 1 and E 5 respectively.

Figure 32 shows the shallow layer obtained when the first set of iron phosphate treated components were annealed.

6.3. Conclusions

A comparison of the structures obtained in series E5B indicated that the layers produced by the commercial phosphate coating with commercial lubricant and by the pure iron phosphate coating with sodium hydroxide top coating were qualitatively similar, and this similarity was confirmed by the quantitative results (Table 16).

The results from Section E 1 indicated that with the light weight iron phosphate coating a layer was formed which was qualitatively similar but very much shallower in depth. The iron phosphates produced in the two experiments differed only in thickness, and this indicates that the depth of diffusion is dependant upon the quantity of material present on the surface, other factors being equal.
7. **INFLUENCE OF ZINC**

7.1. **Procedure**

In series E1, E4 and E5 a number of comparisons were made between electroplated zinc and iron phosphate. In other tests (E3 and E8) a zinc phosphate coating was deposited from a pure solution and compared with the iron phosphate coating. Type (a) test piece samples (Fig. 29) were heated to 950 and 1050°C in dry and wet hydrogen and in air, examined visually and metallographically, pickled and re-examined. Variations in weights were noted at the different stages. Tensile tests were also carried out, but these are discussed in a later section (Section 14). The tests also examined the effect of different top coatings including commercial soap, stearic acid and graphite. Full details of the test conditions are given in Table 15.
7.2. Results

Table 16 gives the results of metallographic examination of specimens from series El, while Table 17 gives the results of visual and gravimetric examination. Corresponding details from series E4 are given in Tables 18 and 19, from series E5 in Tables 20 and 21 and from series E8 in Tables 22 and 23.

The microstructure obtained when a zinc plated specimen is heated in hydrogen to \(950^\circ C\) for 20 minutes is shown in Fig. 33. A specimen coated with zinc plus Bonderlube 235 and heated similarly is shown in Fig. 34, while the structure of a zinc plated specimen heated in air for 20 minutes at \(950^\circ C\) is shown in Fig. 35. These samples were all taken from series El and the structures indicated that intergranular penetration occurred when zinc plated specimens were heated and that the type of atmosphere and the presence of a soap layer had relatively little effect on the form of the attack. The characteristic globular form of the inclusions and the diffused layer in the metal phase present in phosphated samples after annealing were absent from all of the zinc plated specimens.
In series E8 zinc phosphate coatings and iron phosphate coatings were treated with sodium hydroxide and heated to 1050°C. The structures produced by both types of coating were very similar (Figs. 37 and 38).

The quantitative measurements summarised in Tables 17, 19 and 21 indicate that both the zinc plated and the phosphated samples lose weight on annealing in a reducing atmosphere, and both are attacked and lose weight during subsequent pickling in inhibited acid. The weight loss on pickling of phosphated samples is, however, much higher than the corresponding weight loss of zinc plated samples. The phosphated and annealed specimens were nearly always covered with a black smut similar to that shown in Fig. 20.

Sample P99 (series E8) was coated with zinc phosphate and sodium hydroxide, annealed at 1050°C for 30 minutes in wet hydrogen, and was analysed by the Cambridge X-ray scanning microanalyser. Neither zinc photograph nor slow line scan showed any increase in zinc concentration in the surface layer (Fig. 39). It was concluded that if zinc was present in the sample it was less than 0.25%
and could not be adequately displayed by the method. Other methods of analysis also failed to reveal zinc.

Specimen 15B was coated with zinc phosphate and heated to approximately 950°C in an induction coil, in air. A visual examination showed that the upper surface was covered with a fluffy layer of zinc oxide (Fig. 40). As the volatilisation temperature of zinc oxide is very high it is evident that zinc was driven off from the coating as metal which oxidised in contact with air. The fact that no zinc has been detected analytically in the surface layer after annealing coupled with the results of this test indicate that zinc is lost from the coating by volatilisation during the annealing treatment.

7.3 Conclusions

(1) When zinc plated specimens, with or without a top coating of soap or other sodium compound are annealed in a reducing or oxidising atmosphere, a form of intergranular penetration is produced which is metallographically different from the reaction produced by a zinc phosphate coating under similar

81
conditions, and there is no evidence of diffusion through the metal phase.

(2) Several methods of analysis, including the electron probe microanalyser, have failed to reveal any increase in zinc concentration in the diffused surface layer. There is evidence that zinc boils from a phosphate coating heated in air to a similar temperature range. It is probable that the zinc boils off from the coating under reducing conditions also and plays no part in the reaction.
8. INFLUENCE OF PHOSPHORUS

8.1. Procedure

The tests described in sections 6 and 7 served to establish the role of phosphorus in the reaction, as they indicated that the effect could be produced with pure iron phosphate.

Electron microprobe investigations into the phosphorus concentration of the surface layer were also carried out, and the effect of phosphoric oxide powder heated on a steel plate was examined in Series E9.

8.2. Results

Experimental results are tabulated as reported in Section 7.

A comparison of figs. 37, 38, 41 and 42 indicates the similarity of all specimens with phosphate coating whether zinc is present or not and the evidence from the tables confirms that, given similar quantities per unit area of the deposited coatings, the weight loss on annealing, the depth of penetration of the diffused metal phase and of the non-metallic phase, and the weight loss
on subsequent pickling are all similar for the different types of phosphate coating. The characteristic formation of black smut on pickling also distinguishes the phosphated samples.

Stead's reagent which was developed as a specific test for variations in phosphorus content, was found to differentiate sharply between the diffused surface layer and the underlying steel (Figs. 41 and 42) in phosphated samples after annealing but not in zinc plated specimens (cf. Fig. 36).

In series E9 phosphorus pentoxide on a steel plate was heated to 1050°C in wet hydrogen for 20 minutes. This produced a deep layer of diffused metal phase containing numerous inclusions as well as traces of phosphide eutectic at the extreme surface (Fig. 43).

Sample P99 (Series E8) was examined with the Cambridge X-ray scanning microanalyser (see section 7.3).

A phosphorus photograph revealed a high concentration of phosphorus in the non-metallic inclusions (Fig. 81),
and it was estimated that the phosphorus content of this slag phase was of the order of 15 - 20%. A slow line scan across the diffused layer indicated that the phosphorus concentration at the surface was nearly six times as high as the average concentration in the interior of the specimen, and decreased gradually to the average concentration at a depth corresponding well with the visual depth of the diffused layer. The slow line scan is reproduced in Fig. 44. The phosphorus content of the steel is 0.028% and this would indicate, with a ratio of 5.6 to a surface phosphorus content of approximately 0.16% phosphorus. The manganese scan shown in Fig. 44 is discussed subsequently (Section 11.2).

8.3. Conclusions

(1) The surface reaction is produced by a number of phosphate coatings.

(2) Electron probe microanalysis of a typical layer revealed a phosphorus concentration in the slag phase of 15 - 20% and a surface concentration in the metal phase of about 0.16%, six times the average phosphorus content of the steel. Stead's
reagent also indicated an increase in phosphorus content in the surface layer.

(3) With a large concentration of phosphorus at the surface, produced by heating steel in contact with P_2O_5, traces of phosphide eutectic were visible in the microstructure at the surface of the specimen.
9. INFLUENCE OF ORGANIC MATTER AND CARBON

9.1. Procedure

In test series E4, samples coated with zinc or with iron phosphate were covered with graphite or stearic acid, annealed and examined in the usual way.

9.2. Results

The test results are given in Tables 18 and 19.

It was found that the addition of carbon in the form of graphite or of stearic acid produced an appreciable carburising effect on the surface of the steel, but did not effect the penetration of either zinc or phosphorus in any way. The diffused phosphorus layer was almost free from carbon after slow cooling although the underlying areas were enriched with this element.

9.3. Conclusions

The results of this series of tests indicate that the stearate radical in the soap lubricant does not play any important part in promoting the reaction between phosphate and steel.
10. **INFLUENCE OF SODIUM**

10.1. **Procedure**

In Series E5, sodium hydroxide coatings were compared with commercial soap, over commercial and pure iron phosphate undercoats. In Series E8, sodium hydroxide was used as a top coating over iron and zinc phosphates. In Series E9 sodium carbonate was used as a top coat over zinc and iron phosphate coating on tensile test pieces. The results of these mechanical tests are given in a later section. In Series E9 a mixture of sodium phosphate and phosphorus pentoxide heated on a steel plate, was compared with phosphorus pentoxide alone. Test conditions are given in Table 15.

10.2. **Results**

The results of Series E5 are recorded in Tables 20 and 21, those for series E8 in Tables 22 and 23, these results should be studied in conjunction with the results from Series E1 for samples treated with phosphate coatings only and with phosphate/lubricant coatings (Tables 16 and 17).
These results indicate an increased depth of diffused layer when sodium is present, and together with the visual appearance indicate that surface melting has taken place (Fig. 45). This is reported in the tables as 'resolidified'. A section through the resolidified layer shows it to consist of the diffused surface layer carrying a zone of non-metallic inclusions at some distance below the surface. The layers produced by heating specimens coated with the commercial phosphate/lubricant coating were closely reproduced by heating specimens coated with pure iron phosphate and sodium hydroxide under similar conditions (compare Figs. 46 and 47). The effect of heating specimens treated with sodium hydroxide only in reducing atmospheres was to produce a pitted surface with no evidence of diffusion (Fig. 48).

A mixture of 21% sodium phosphate (NaPO₃) and 79% phosphorus pentoxide heated in contact with a steel plate at 1050°C in wet hydrogen, produced the result shown in Figs. 49 and 50, which show clearly that surface melting has taken place. A section through the resolidified mass is shown in Figs. 51 and 52 which reveal that a large
quantity of phosphide eutectic was produced and, at the interface between the eutectic and the steel, the diffused layer containing non-metallic inclusions was present. As shown in Fig. 43, 100% phosphorus pentoxide under the same conditions produced a similar diffused layer but with only traces of eutectic. The main effect of sodium appears to be to increase the amount of phosphide eutectic formed at 1050°C either by lowering the melting point of the eutectic or by retaining phosphorus as a more stable compound. The diffusion of phosphorus from the eutectic area into the adjacent ferrite can account for the surface layers observed which had the physical appearance of metal which had melted and re-solidified, and yet have a metallographic structure indicating a much higher melting temperature than that to which the samples were subjected.

In Series E3, a sheet metal test piece T20 was treated with iron phosphate and sodium carbonate before heating in wet hydrogen at 1050°C. Fig. 53 shows the surface after heating at 1050°C for 10 minutes, when it had a bright slightly roughened appearance, and was covered with black, glassy slag globules. The specimen was reheated to the same temperature for a further period of 10 minutes, (Fig. 54), after which the black slag globules were replaced by bright metallic globules, similar to those
of Figs. 45. Fig. 55 shows the same specimen after pickling 15 minutes in inhibited acid. The surface is generally roughened and shallow pits are present in positions corresponding to the location of the bright metallic globules.

10.3. Conclusions

(1) The presence of a sodium salt as an addition to the phosphate coating encourages the formation of a molten layer at the surface of the specimen at treatment temperatures of 1050°C.

(2) The mechanism of formation appears to involve three stages. At first a molten slag is present at the surface of the component; after further heating a layer of molten phosphide eutectic is present at the extreme surface, with globules of slag or oxide in a sub-surface zone; continued heating leads to a reduction in phosphorus concentration at the surface through diffusion so that the eutectic is replaced by a phosphorus rich ferrite which still has the topographical conformation of melted and re-solidified material.
11. INFLUENCE OF MOISTURE IN THE FURNACE ATMOSPHERE

11.1. Procedure

The test series E5 already discussed in section 10 also dealt with the effect of moisture, parallel tests being carried out in hydrogen dried to a dew point of -20°C and saturated to a dew point of +23°C.

11.2. Results

Metallographic results (Table 20) and gravimetric and visual observations (Table 21) indicate that the depth of the diffused phosphorus rich layer in the metal phase is not significantly affected by the moisture content of the atmosphere, but that the extent of the non-metallic inclusion layer is reduced at low dewpoints. Similarly coated specimens heated in wet and dry hydrogen are illustrated in Figs. 46 and 57 and in Figs. 42 and 59.

Diffused layers produced in dry hydrogen are relatively free from non-metallic inclusions or tend to contain numbers of very small inclusions. The layers produced in wet hydrogen are deeply riven, almost disrupted with heavy concentration of non-metallic inclusions.
The sample submitted for electron probe microanalysis (P99) had been annealed in untreated hydrogen (Dew Point + 15°C). The results showed an unexpected variation in manganese content. The slow line scan, reproduced as line 3 in Fig. 44, showed the general level of manganese in the metal phase of the phosphorus rich diffused layer to be only about half the average manganese level, but in the non-metallic phase the concentration of manganese was extremely high. This concentration is shown in the manganese X-ray photograph (Fig. 82). The manganese content of the non-metallic inclusions was estimated as over 10%. Since the phosphating solutions employed contained no manganese this concentration of manganese must have come about through the migration of this element from the surrounding areas of phosphorus rich metal layer into the non-metallic phase. The apparent influence of moisture content of the furnace atmosphere on the quantity of non-metallic phase present suggests that the mechanism may be analogous to the internal oxidation which has been observed in carburising atmospheres (41, 42). It is also possible that the liquid slag formed during the reaction acts as an oxygen carrier in a way similar to the role of vanadium pentoxide slags in oxidising atmospheres (64).
11.3. Conclusions

(1) The amount of non-metallic inclusion present in the diffused phosphorus rich layer appears to be influenced by the oxidising potential of the furnace atmospheres as determined by its water content.

(2) In the diffused metal layer manganese is preferentially oxidised and absorbed into the non-metallic slag phase, leading to an enrichment of the non-metallic globules in manganese and a corresponding impoverishment of the surrounding areas.
12. THE DIFFUSION OF THE REACTION COATING

12.1. Procedure

In Series E.8 two sets of test blanks (Fig. 29a), one coated with iron phosphate and sodium hydroxide, the other with zinc phosphate and sodium hydroxide were heated to 1050°C in an atmosphere of hydrogen (Dewpoint 17°F) and held for times varying from 1 to 90 minutes. The rate of penetration of the diffused phosphorus layer and of the zone of non-metallic inclusions was determined. The reaction begins below 1050°C and the samples treated for 1 minute were intended to provide an estimate of this error.

12.2. Results

The progress of the reaction can be followed visually by referring to Figs. 62 and 63 which show the microstructures existing after various lengths of time with the two types of coating. The phosphorus rich diffused layer increases in depth with time with both types of coating. The non-metallic inclusions appear and penetrate gradually inwards at a much slower rate. There is some difference in the appearance and mobility of the inclusions formed from the two types of coating, but these differences may
be related more to the physical and mechanical properties of the coatings at temperature than to chemical differences between them.

The average of a number of determinations on each specimen of the depth of decarburisation, depth of diffused layer and maximum depth of penetration of the non-metallic inclusions are plotted against treatment time in Fig. 64. The similarity between the two families of curves confirms that the diffusing substances are the same irrespective of the presence of zinc.

12.3 Conclusions

(1) The test results confirm that both the phosphorus rich metal layer, and the non-metallic phase, diffuse inwards with time although at different rates.

(2) The rate of diffusion in the metal phase is closely similar whether the original coating is iron phosphate or zinc iron phosphate.

(3) There are some differences in the form and mode of penetration of the non-metallic
phase according to whether the originating coating is iron phosphate or zinc iron phosphate. As no zinc was detected in the slag this is likely to be due to the physical rather than the chemical characteristics of the slag.
13. **EFFECT OF THE REACTION COATING UPON SUBSEQUENT PICKLING**

13.1. **Procedure**

The samples from series E.8, discussed in the preceding section were pickled in inhibited 10% sulphuric acid for 15 minutes and the loss in weight recorded. They were then examined metallographically and the remaining part of the specimens identified with the suffix letter a, reweighed and re-pickled for a further 60 minutes, before final weighing and examination.

13.2. **Results**

The weight losses after pickling for 15 minutes are plotted against time of annealing in Fig. 65. The upper curve is for the iron phosphate/sodium hydroxide coated specimens and the lower curve for the zinc-iron phosphate/sodium hydroxide coated specimens. With both types of coating the weight loss increased with increasing annealing time up to a maximum at 30 minutes for iron phosphate (phosphorus layer depth .13 mm) and at 10 minutes for zinc iron phosphate (phosphorus layer depth .12 mm) and then decreased.
After the first pickle there was little visual sign of attack, but the microexamination and weight losses indicated that sub-surface attack was taking place.

The weight losses after pickling for a total of 75 minutes are shown in Fig. 66 plotted against annealing time. The weight losses shown have been adjusted to take account of the removal of a part of the sample for micro-examination after the first pickle, assuming no attack on the exposed clean metal. The actual and adjusted weight losses are shown in Table 26. The upper curve in Fig. 66 is for the iron phosphate/sodium hydroxide coated specimens and the lower curve for the zinc iron phosphate/sodium hydroxide coated specimens. The weight losses are of a greater order of magnitude than those found after 15 minutes, confirming that the inhibitor in the acid is rendered ineffective by the surface layer. The weight losses with both types of coating tended to decrease with longer annealing times, due probably to a reduction in phosphorus concentration.
Metallographic examination of the pickled specimens makes the mechanism of the acid attack clearer (Figs. 67-72). The acid first penetrates in a series of deep pits to the diffused layer interface (Fig. 71, 72). As no non-metallic inclusions were observed in any of the pickled specimens it appears likely that the inclusions dissolve readily in the acid to form the nuclei of the deep pits observed. The attack progresses along the interface leaving isolated islands of undissolved metal in the layer (Figs. 69, 70). Eventually when the phosphorus rich layer is completely dissolved a relatively smooth surface is left (Fig. 68).

13.3. Conclusions

(1) The immunity of steel to attack by inhibited 10% sulphuric acid is destroyed by the presence of the phosphorus rich layer and solution will continue until this layer is completely dissolved.

(2) The solution rate can be reduced by increasing the depth of diffusion through prolonged annealing. If the reaction with the acid
went to completion, the loss of weight on a specimen with increased diffusion would, however, be ultimately greater.

(3) The acid first dissolves the inclusions to form deep pits extending to the interface of the phosphorus layer. General solution of the phosphorus rich layer then occurs.

(4) After the normal pickling time of 15 minutes the reaction is only partly complete and the surface is deeply fissured and pitted.
14. EFFECT OF THE REACTION COATING AND OF THE SURFACES PRODUCED BY PICKLING ON SUBSEQUENT DUCTILITY

14.1. Introduction

To test the effect of the surface reactions on mechanical properties it was considered that a tensile test would be the most appropriate since the deformed surface of the test piece would not be affected by contact with the deforming tool, as in compression or extrusion tests, and the interpretation of the results would be correspondingly simpler.

14.2. Procedure

In the first series of tests carried out (Series E 3/8) 0.564" dia. tensile test pieces were used. The effects of commercial phosphate, soap and contact with nickel-chromium wire during annealing and of pickling, rephosphating and lubricating after annealing were compared. Details are given in Table 15.

These tests showed that there was surface cracking on specimens coated before annealing, but the effect on the overall mechanical properties was small. A second series of tests was therefore carried out using test
pieces cut from sheet to increase the ratio of surface area to volume (Series E 3/b).

These tests compared zinc phosphate with and without a top coating of sodium carbonate; and iron phosphate, with and without a top coating of sodium carbonate, contact with Nickel Chromium Wire during annealing and pickling after annealing (Table 15).

14.3. Results

The tensile test results are given in Table 27. The maximum stress (MS) is the maximum load divided by the original cross-sectional area. The true U.T.S. is the final breaking load divided by the final cross-sectional area, measured after fracture. The results of the first series T1 - 12 showed no real difference in test results between the different treatments. The surface of the specimens which were phosphated before annealing showed a series of shallow circumferential tears or cracks in the necked area of the test piece, which were absent in the specimens annealed without a surface coating. Where a nickel-chromium wire was bound over a phosphate or phosphate-soap coating areas of local welding and alloying occurred.
In the second series of tests, T13 - 24, samples which were phosphated or phosphated and lubricated before annealing showed a considerable loss of elongation and a drop in reduction of area (Table 27). Although the maximum stress was about the same for treated as for untreated specimens, the smaller reduction in area meant that the true U.T.S. was also reduced. Pickling the coated samples after annealing did not appear to improve the mechanical properties.

Samples which were phosphated before heat treatment developed transverse surface cracks on tensile testing (Figs. 73 - 76). Fig. 73 shows specimen T.23, annealed without coating which has a roughened surface but shows no evidence of cracking. The extent of necking is also evident. Fig. 74 shows sample T.13 annealed after coating with zinc-iron phosphate and transverse cracking in the vicinity of the fracture, together with reduced necking are visible. Fig. 75 shows sample T.21, coated with iron phosphate and bound with nickel chromium wire before annealing. Here a secondary fracture from a point where local melting and alloying with the wire has occurred is running at an angle into the main fracture.
Fig. 76 shows specimen T.18 coated with iron phosphate and annealed and then pickled before testing. It will be seen that pickling for the standard cycle time has done nothing to reduce transverse surface cracking.

Surface hardness tests, (Table 29), show that the phosphorus rich layer formed in annealing is up to 100 D.P.N. harder than the untreated metal. Pickling for the standard cycle time apparently reduces the hardness to the level of the untreated steel. Where the alloying with nickel chromium has occurred the hardness can be as high as 445 D.P.N.

14.4. Conclusions

(1) The reaction coating produced by heating specimens coated with phosphate or phosphate/lubricant to 950°C or 1050°C in a reducing atmosphere is harder and less ductile than the bulk material leading to the formation of transverse cracks on elongation. If the surface area of the specimen is high in relationship to its bulk, the overall mechanical properties of the sample are affected.
(2) Pickling for the standard time removes the hard layer at the extreme surface, but does not eliminate the transverse cracking.

(3) Contact between phosphated steel surfaces and nickel-chromium alloys during the heating cycle can lead to local alloying and the formation of very hard spots which act as fracture nuclei.
15. **ANNELING IN A VACUUM**

15.1. **Procedure**

Vacuum annealing to dissociate the coating and volatilise the reactive constituents was examined in two series of tests/10⁻¹ Torr, and 10⁻⁵ Torr with temperatures of 650°C, 950°C and 1050°C. The test pieces were coated with commercial phosphate or with commercial phosphate and soap. One zinc plated specimen was also treated in low vacuum at 1050°C.

15.2. **Results**

The results of metallographic examination are given in Table 24. At 650°C there was no appreciable reaction between the coating and the base metal. At 950°C and 1050°C in a low vacuum (10⁻¹ Torr) the diffused phosphorus layer was present and extended to a depth comparable to that found in specimens heated in a reducing atmosphere. The layer was relatively free from the zone of non-metallic inclusions and in this respect resembled samples heated in an atmosphere of dried hydrogen (See Fig. 83).

Specimens heated to 950°C and 1050°C in a high vacuum (10⁻⁵ Torr) showed some diffused phosphorus layer and rare
non-metallic inclusions, but the depth of penetration was very sharply reduced. It seems likely that part of the reactive coating had been lost from the surface through dissociation or evaporation. A feature of the tests was the heavy decarburisation experienced on specimens heated to 950°C and 1050°C in high vacuum. The vapour pressure of elemental carbon at these temperatures is so low that it could only have been lost as carbon monoxide. It is possible that the CO was formed in a reaction between the carbon and the phosphate coating.

Visual examination showed that after heating at 650°C a recrystallisation of the phosphate coating had occurred, probably due to dehydration, (30). After heating at 950°C the surface was partially transformed to metal. After heating at 1050°C the transformation was complete; Similar changes occur in the presence of soap lubricant.

15.3. Conclusions

(1) Heating specimens coated with commercial phosphate and phosphate-soap coatings in a moderate vacuum to 950°C and 1050°C resulted in a reaction similar to that which takes place in a reducing atmosphere.
If the pressure was reduced from $10^{-1}$ to $10^{-5}$ Torr, the depth of penetration of the reaction products into the steel was substantially reduced, indicating that part of the coating was driven off before reacting with the steel.

Although an improvement would result from heat treating in a high vacuum, complete volatilisation of the coating is not effected and so the more expensive treatment could not be justified economically.
16. COMPARISON OF METHODS OF STRIPPING THE PHOSPHATE COATING

16.1. Procedure

The hot alkaline solution normally employed for stripping was compared with an alternative NaOH/NaCN solution recommended by Eisler (62), (Series E10). Test pieces coated with commercial phosphate and with phosphate + soap were treated for 20 minutes at 70°C in 20% NaOH solution or for 10 minutes in a cold solution containing 150 g/l NaOH and 75 g/l NaCN. The weight loss after stripping was recorded, residual phosphate was removed by solution in concentrated HCl inhibited with 20 g/l Sb₂O₃ (65), and the phosphate determined by precipitation and ignition to magnesium pyrophosphate (61).

Samples with phosphate and phosphate-soap coatings stripped in both types of solution were annealed in hydrogen at 1080°C for 20 minutes and examined in the usual way.

16.2. Results

The weight losses on the test samples after stripping in the two solutions are compared with the total coating weights (determined on blank specimens), in Table 30. The loss in weight resulting from stripping in hot 20% NaOH
solution without scrubbing was appreciably less than the total coating weight. The residue was rich in phosphate. Weight loss in NaOH/NaCN solution was very close to the total coating weight and the residual phosphate on the samples after stripping was negligible.

Samples which were stripped in NaOH before annealing showed an irregular diffused phosphorus layer containing a number of non-metallic inclusions, (Fig. 84).

Samples which were stripped in NaOH/NaCN solution before annealing had a surface structure slightly decarburised but free from the diffused phosphorus layer and from non-metallic inclusions, (Fig. 85).

Annealed samples were pickled and the weight losses are recorded in Table 31. Samples which had been stripped in the hot 20% NaOH solution before annealing suffered a considerable weight loss on pickling. The attack on samples which had been stripped in the NaOH/NaCN solution before annealing was negligible.

16.3. Conclusions

(1) Tests show that stripping either a phosphate coating
only or a phosphate/lubricant coating in a hot 20% NaOH solution results in only incomplete removal of the coating if no supplementary scrubbing is used. The residual coating will react with the surface on subsequent annealing.

(2) Stripping either a phosphate coating only or a phosphate-lubricant coating by immersion in a cold solution containing 7.5% w/v NaCN and 15% w/v NaOH results in an almost complete removal of the coating and no surface reaction occurs on subsequent annealing.
17. DISCUSSION

17.1. Summary of Results Obtained

The principal results of the tests were as follows:

1. The reaction between phosphate coating and steel surface during annealing was similar in nature and extent on undeformed as well as deformed specimens.

2. The reaction product consisted of a non-metallic phase dispersed in a metallic matrix, diffused into the steel surface.

3. The maximum depth of penetration of the reaction product was dependant on the concentration of reactant at the surface, other factors being equal.

4. The reaction was not significantly influenced by any of the minor constituents present in the phosphate or lubricant coating.

5. Zinc did not play any important part in the reaction.

6. The characteristic surface reaction product under investigation was produced by a number of coatings containing phosphorus and analysis showed a high phosphorus concentration in the non-metallic phase and a phosphorus gradient from surface to core in
the diffused metal layer. Phosphide eutectic was present in samples heated at 1050°C.

(7) The stearate radical in the soap-lubricant did not affect the reaction between phosphate and steel.

(8) The enhanced activity of a phosphate coating when soap was present was due to the sodium ion which encouraged the formation of a molten surface layer at temperatures of 1050°C, consisting initially of a molten slag which progressively changed to a phosphide eutectic then to a phosphorus rich ferrite containing non-metallic inclusions.

(9) The amount of non-metallic inclusion present in the diffused layer was influenced by the oxidising potential of the furnace atmosphere, as governed by its water content, within the limits investigated.

(10) In the diffused layer, manganese was preferentially oxidised and absorbed into the non-metallic phase.
(11) The phosphorus rich metal layer and the zone of non-metallic inclusions diffused inwards although at different rates.

(12) The immunity of the steel to attack by inhibited 10% sulphuric acid was destroyed by the presence of the phosphorus rich layer and solution continued until this layer was completely dissolved. A partially dissolved layer produced after the normal pickling time contained numerous deep pits due to preferential solution of the non-metallic phase.

(13) The surface layer was harder and less ductile than the bulk material and transverse surface cracks were formed on stretching the material. Pickling for the standard time did not eliminate the transverse cracking. Hard spots formed by reaction with the nickel-chromium furnace material accentuated the cracking.
(14) Annealing coated specimens in a moderate vacuum resulted in a reaction similar to that produced in a reducing atmosphere. In a high vacuum the depth of penetration was substantially reduced, indicating that part of the coating was driven off before reacting with steel.

(15) If the normal alkaline stripping solution was replaced by a 7.5% NaCN/15% NaOH solution, the coating was entirely removed before heat treatment, thus preventing any surface reaction.

17.2. General Discussion of Results

The results of the tests indicated that, of the different elements present in the phosphate-soap coating, phosphorus and sodium reacted with the steel on heating in a reducing atmosphere to produce a molten slag at 950 - 1050°C, from which the phosphorus passed into the metal phase and the non-metallic phase became enriched with manganese. Although previous work has been carried out on phosphorus rich slags containing sodium, this related to reactions in air at steelmaking temperatures and could only provide a rough guide to the reactions taking place in the present tests. Wentrup (76)
investigated the Fe-P\textsubscript{2}O\textsubscript{5} system under oxidising conditions and much work has also been done on the lime containing phosphate slags and the equilibrium between these slags and iron in recent years by Tromel and his co-workers (66 - 69). The corresponding sodium phosphate slags were studied by Oelsen and Weimer (70) and more recently by Turkdogan and Maddocks (71 - 73). The relationship between manganese, iron and phosphoric oxide were investigated by Oelsen and Maetz (74) and the Mn-O System by Halm and Muan (75). Wentrup (76) presented a diagram for the iron oxide - P\textsubscript{2}O\textsubscript{5} system in contact with air showing eutectics between 2Fe\textsubscript{2}O\textsubscript{3}P\textsubscript{2}O\textsubscript{5} and Fe\textsubscript{2}O\textsubscript{3}P\textsubscript{2}O\textsubscript{5} and between Fe\textsubscript{2}O\textsubscript{3}P\textsubscript{2}O\textsubscript{5} and 2Fe\textsubscript{2}O\textsubscript{3}3P\textsubscript{2}O\textsubscript{5}, the eutectic temperature in both cases being below 1000°C. Tromel and Schwerdtfeger (69) examined the same system in contact with the metal phase and found that, where the stable iron oxide was FeO, liquid was present to a minimum eutectic temperature of 940°C, the eutectic composition being 38% P\textsubscript{2}O\textsubscript{5}. Turkdogan and Maddocks (73) examined the binary Na\textsubscript{2}O - P\textsubscript{2}O\textsubscript{5} system and reported eutectics at 944°C (70 mole % Na\textsubscript{2}O) and at 546°C (57 mole % Na\textsubscript{2}O). The ternary system Na\textsubscript{2}O - P\textsubscript{2}O\textsubscript{5} - FeO was shown to contain a liquid miscibility gap by Oelsen and Weimer (70) and to be qualitatively very similar to the system CaO-P\textsubscript{2}O\textsubscript{5} - FeO. For this
reason diagrams presented by Tromel Fix and Fritz (68) showing the effect of CaO slag composition and temperature on the phosphorus and oxygen contents of the equilibrium metal phase are likely to represent also the relationships existing with a sodium oxide slag. These diagrams in conjunction with the equilibrium diagrams suggested that a slag rich in phosphoric oxide would have a relatively low melting point and be in equilibrium with a high phosphorus content in the metal phase.

Turkdogan and Maddocks (73) also drew attention to the high vapour pressure of both Na₂O and P₂O₅, which limited the range of composition investigated in the Na₂O-P₂O₅ binary system to between Na₂O-P₂O₅ (50 mole % Na₂O) and 3Na₂O-P₂O₅ (75 mole % Na₂O). It was evident that the compounds formed between these limits were more stable, through having a reduced vapour pressure, than either of the pure substances. It could, therefore, be said that one of the effects of adding sodium oxide to phosphoric oxide was to reduce the loss of phosphorus by volatilisation at elevated temperature through reducing the vapour pressure. It was considered that this was the most probable explanation of the influence of sodium soap on the reaction between phosphate and steel. Although
pyrophosphates are extremely stable when heated in an oxidising atmosphere, this was evidently not the case in a reducing atmosphere and phosphate samples detached from the steel surface and heated in this way were in fact found to decompose to a magnetic powder which gave strong α-iron lines on X-ray examination (Fig. 79). Under these circumstances the phosphorus must have been present as an elemental or oxide ion, the vapour pressure of which would result in considerable loss by evaporation unless a compound of lower vapour pressure could be formed.

The phosphorus rich slag formed on the steel surface was in equilibrium with the metal and with the atmosphere. Under the very reducing conditions of the treatment much of the phosphorus evidently passed from the slag into the metal phase and diffused inwards into the steel to form a diffuse phosphorus rich layer on the surface. The small atomic size difference between iron and phosphorus (13%) and the partial solubility which existed would favour the formation of such a layer (47).

The appearance of non-metallic globules in the diffused layer, which are enriched in manganese, indicated that internal oxidation was also taking place. The solutions
used to produce the zinc and iron phosphate coatings contained no manganese, and this was obtained entirely from the surrounding matrix. A similar phenomenon was observed by Hultgren and Hagglund (41), in steels exposed to a carburising atmosphere. The oxidation indicated that the furnace atmosphere, although reducing to iron, had an oxidising potential sufficiently high to oxidise manganese (40, 42). With the hydrogen atmospheres used in the tests, the oxidising potential was governed by the $\text{H}_2\text{O}/\text{H}_2$ ratio and it was found that the amount of non-metallic inclusions present was in fact related to the moisture content of the atmosphere. The oxygen rich layer was found to increase in depth with increasing time at temperature, although the rate of diffusion was slower than that of phosphorus. This may have been due to the low oxygen potential of the atmosphere and the resultant shallow concentration gradient.

When sodium compounds were present at the surface, together with the phosphate layer, the zone of non-metallic inclusions was more pronounced and extended to a greater depth, possibly due to the liquid slag acting as an oxygen carrier, as in the $\text{V}_2\text{O}_5 - \text{NaVO}_3$ system (64).
The loss of immunity of the reacted surface layer to attack by inhibited acid was partly due to the presence of the non-metallic inclusions, which were readily soluble. The continued solution of the phosphorus-rich layer may have been an electrolytic effect. The action of the Stead's reagent, which deposits copper on the areas low in phosphorus, indicated that the phosphorus-rich surface was anodic to the base metal.

17.3. **Significance of Results**

Many of the phenomena found in the course of the tests bore a close resemblance to the features observed on components when cracking was experienced during extrusion. In particular, the heavy weight loss and pitting during pickling were reproduced by the test conditions. The abnormally heavy coating weights produced on re-phosphating can now be seen to be due to the incorporation of the black smut which was formed in large quantities when the phosphorus rich layer was pickled. The transverse surface cracking observed on extrusions was also paralleled by the similar cracking observed on tensile test pieces during the tests.

In order to prevent the hard and unsound phosphorus rich layer causing difficulties in subsequent extrusion, a number...
of possible courses of action could be envisaged:

(1) Heat treatment at sub-critical annealing temperature. This has the disadvantage of producing an unsatisfactory microstructure with a zone of coarse grain size.

(2) Heat treatment in air at high temperature. This would lead to long pickling times for complete scale removal and an uneconomic loss of metal.

(3) Complete removal of the phosphorus rich layer by pickling. This again would require long pickling times and lead to heavy metal loss.

(4) Volatilisation of the coating during the early stages of annealing by heating in a vacuum. This procedure was found to be only partially successful even when an expensive, high vacuum technique was employed.

(5) Complete removal of the coating before heat treatment. This procedure was found to be entirely
successful in preventing the formation of a phosphorus rich layer, but a more efficient stripping solution than that normally employed is required. A sodium cyanide/sodium hydroxide solution has been found to fulfil the requirements.

It is concluded that the best answer to the problem is to use a 7.5% sodium cyanide, 15% sodium hydroxide solution to remove the phosphate/lubricant coating before interstage annealing.
18. CONCLUSIONS

The heating of steel components coated with commercial zinc phosphate in a reducing atmosphere at temperatures of 950 - 1050°C results in the formation of a diffused phosphorus rich layer at the steel surface containing non-metallic inclusions.

If a sodium based lubricant is also present, surface melting occurs and the penetration of both phosphorus and non-metallic inclusions is increased.

The reaction layer is attacked by the inhibited sulphuric acid pickle which precedes rephosphating in the production cycle. After the normal pickling time the layer is partially dissolved giving rise to a deeply fissured surface.

Both the reaction layer and the partially pickled reaction layer reduce the ductility of the steel surface and transverse surface cracking is produced when the more ductile core deforms plastically.

The most suitable method of preventing the formation of the reaction layer is by complete removal of the phosphate.
lubricant coating using a stripping solution containing 7.5% sodium cyanide and 15% sodium hydroxide.
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Table 1.
Sequence of operations in the Bonderising Process

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
<th>Strength</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Degrease</td>
<td>4 oz/gal.</td>
<td>88 - 93°C</td>
<td>10 - 15 min.</td>
</tr>
<tr>
<td></td>
<td>Alkali Cleaner</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 - 5 min.</td>
</tr>
<tr>
<td>3.</td>
<td>Inhibited Sulphuric Acid Pickle</td>
<td>10% v/v</td>
<td>60 - 66°C</td>
<td>10 - 15 min.</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
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<td>4.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 - 5 min.</td>
</tr>
<tr>
<td>5.</td>
<td>Hot water rinse</td>
<td>-</td>
<td>74 - 79°C</td>
<td>2 - 5 min.</td>
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<td>6.</td>
<td>Zinc Phosphate (Bonderite 181X)</td>
<td>70 points</td>
<td>83 - 85°C</td>
<td>10 - 20 min.</td>
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<td>7.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 - 5 min.</td>
</tr>
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<td>8.</td>
<td>Conditioning Chemical</td>
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<td>9.</td>
<td>Lubricant Sodium Stearate (Bonderlube 235)</td>
<td>7% w/v</td>
<td>53 - 58°C</td>
<td>5 - 10 min.</td>
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<td>10.</td>
<td>Drain</td>
<td>-</td>
<td>-</td>
<td>2 - 5 min.</td>
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Table 2. Effect of Annealing Temperature on Extrusion Load.

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<th>Treatment</th>
<th>Hardness Before</th>
<th>Hardness After</th>
<th>Load Indicated</th>
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<tbody>
<tr>
<td>1. 1130°C Atmosphere normalise.</td>
<td>163 BHN</td>
<td>121 BHN</td>
<td>240-270 tons</td>
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<td>2. 950°C</td>
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<td>123 BHN</td>
<td>255-270 tons</td>
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<tr>
<td>3. 720°C Anneal</td>
<td></td>
<td>137 BHN</td>
<td>270-300 tons</td>
</tr>
<tr>
<td>4. 680°C</td>
<td></td>
<td>140-143 BHN</td>
<td>270-285 tons</td>
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Table 3. Test Results on Extruded Cups.

<table>
<thead>
<tr>
<th>No.</th>
<th>Batch</th>
<th>Cracking Severity</th>
<th>Height of Cup (mm)</th>
<th>Base Thickness (mm)</th>
<th>Coating Wt. (mg/dm²)</th>
<th>Slug Weight after (strip gm)</th>
<th>Hardness At rim HV30</th>
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<td>44.76</td>
<td>3.64</td>
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<td>—</td>
<td>140/144</td>
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Table 3 (Cont.)

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<th>No.</th>
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<th>Cracking Severity</th>
<th>Height of Cup (mm)</th>
<th>Base Thickness</th>
<th>Coating Wt. (mg/dm²)</th>
<th>Slug Weight (gm)</th>
<th>Hardness At Rim HV30</th>
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<td>28</td>
<td>3</td>
<td>0°</td>
<td>46.78</td>
<td>3.18</td>
<td>153.3</td>
<td>209.468</td>
<td>141/146</td>
</tr>
<tr>
<td>29</td>
<td>3</td>
<td>0°</td>
<td>46.62</td>
<td>3.30</td>
<td>144.6</td>
<td>209.661</td>
<td>147/150</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>0°</td>
<td>47.16</td>
<td>3.28</td>
<td>165.0</td>
<td>210.797</td>
<td>138/139</td>
</tr>
<tr>
<td>31</td>
<td>3</td>
<td>0°</td>
<td>46.78</td>
<td>3.38</td>
<td>150.9</td>
<td>208.212</td>
<td>150/168</td>
</tr>
<tr>
<td>32</td>
<td>3</td>
<td>0°</td>
<td>46.96</td>
<td>3.30</td>
<td>146.6</td>
<td>210.002</td>
<td>135/135</td>
</tr>
<tr>
<td>33</td>
<td>3</td>
<td>0°</td>
<td>47.24</td>
<td>3.10</td>
<td>197.2</td>
<td>210.185</td>
<td>134/138</td>
</tr>
<tr>
<td>34</td>
<td>3</td>
<td>0°</td>
<td>47.06</td>
<td>3.20</td>
<td>158.4</td>
<td>209.711</td>
<td>140/146</td>
</tr>
<tr>
<td>35</td>
<td>3</td>
<td>0°</td>
<td>47.00</td>
<td>3.36</td>
<td>160.0</td>
<td>209.729</td>
<td>140/161</td>
</tr>
<tr>
<td>36</td>
<td>3</td>
<td>0°</td>
<td>46.48</td>
<td>3.20</td>
<td>152.0</td>
<td>207.697</td>
<td>143/153</td>
</tr>
</tbody>
</table>

The suffix W indicates that the crack, extending round the complete circumference, has widened considerably.
Table 4. Test Results on slugs before extrusion

<table>
<thead>
<tr>
<th>Batch No.</th>
<th>Surface Appearance</th>
<th>Brinell Hardness on top surface (750:5:15)</th>
<th>Hardness on cross section (HV10)</th>
<th>Grain Size ASTM</th>
<th>Coating Wt. mg/dm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Centre</td>
<td>Edge)</td>
<td>106-123</td>
<td>5</td>
</tr>
<tr>
<td>1</td>
<td>Pitted</td>
<td>126</td>
<td>121</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Smooth</td>
<td>121</td>
<td>121</td>
<td>110-128</td>
<td>5</td>
</tr>
</tbody>
</table>
Table 5. Summary of treatment combinations investigated.

<table>
<thead>
<tr>
<th>Treatment Code</th>
<th>No. of Slugs</th>
<th>Type of Strip</th>
<th>Type of Anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>5</td>
<td>Complete strip</td>
<td>1130°C reducing</td>
</tr>
<tr>
<td>CA</td>
<td>6</td>
<td>Soap removed</td>
<td>950°C reducing</td>
</tr>
<tr>
<td>BB</td>
<td>4</td>
<td>Production strip</td>
<td>1130°C reducing</td>
</tr>
<tr>
<td>DB</td>
<td>6</td>
<td>None</td>
<td>1130°C reducing</td>
</tr>
<tr>
<td>DG</td>
<td>3</td>
<td>None</td>
<td>1130°C reducing (M.S. tray)</td>
</tr>
</tbody>
</table>
### Table 6.

**Changes in Weight at Different Stages of Interstage Treatment**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AB</td>
<td>3</td>
<td>.0800</td>
<td>-.0800</td>
<td>-.0046</td>
<td>-.0061</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>.0764</td>
<td>-.0764</td>
<td>-.0050</td>
<td>-.0055</td>
</tr>
<tr>
<td></td>
<td>2B</td>
<td>.0791</td>
<td>-.0791</td>
<td>-.0052</td>
<td>-.0061</td>
</tr>
<tr>
<td>CA</td>
<td>1A</td>
<td>.0805</td>
<td>-.0193</td>
<td>-.0332</td>
<td>-.0458</td>
</tr>
<tr>
<td></td>
<td>2A</td>
<td>.0805</td>
<td>-.0193</td>
<td>-.0334</td>
<td>-.0497</td>
</tr>
<tr>
<td></td>
<td>3A</td>
<td>.0805</td>
<td>-.0193</td>
<td>-.0242</td>
<td>-.1446</td>
</tr>
<tr>
<td></td>
<td>4A</td>
<td>.0805</td>
<td>-.0193</td>
<td>-.0273</td>
<td>-.1186</td>
</tr>
<tr>
<td></td>
<td>5A</td>
<td>.0805</td>
<td>-.0193</td>
<td>-.0295</td>
<td>-.1085</td>
</tr>
<tr>
<td></td>
<td>6A</td>
<td>.0805</td>
<td>-.0193</td>
<td>-.0305</td>
<td>-.1185</td>
</tr>
<tr>
<td>BB</td>
<td>4B</td>
<td>.0805</td>
<td>-.0174</td>
<td>-.0382</td>
<td>-.0924</td>
</tr>
<tr>
<td></td>
<td>5B</td>
<td>.0805</td>
<td>-.0187</td>
<td>-.0321</td>
<td>-.0443</td>
</tr>
<tr>
<td></td>
<td>6B</td>
<td>.0805</td>
<td>-.0174</td>
<td>-.0382</td>
<td>-.0737</td>
</tr>
<tr>
<td>DB</td>
<td>4</td>
<td>.0764</td>
<td>0</td>
<td>-.0588</td>
<td>-.6487</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>.0764</td>
<td>0</td>
<td>-.0588</td>
<td>-.4846</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>.0764</td>
<td>0</td>
<td>-.0588</td>
<td>-.5652</td>
</tr>
<tr>
<td>DG</td>
<td>10B</td>
<td>.0805</td>
<td>0</td>
<td>-.4131</td>
<td>-.1002</td>
</tr>
<tr>
<td></td>
<td>11B</td>
<td>.0805</td>
<td>0</td>
<td>-.7254</td>
<td>-.0962</td>
</tr>
<tr>
<td></td>
<td>12B</td>
<td>.0805</td>
<td>0</td>
<td>-.6270</td>
<td>-.0904</td>
</tr>
</tbody>
</table>
Table 7 - EFFECT OF EXTRUSION ON SURFACE REACTIONS

<table>
<thead>
<tr>
<th>Identification of Samples</th>
<th>Coating Intact</th>
<th>Soap removed</th>
<th>Completely Stripped</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not deformed</td>
<td>A5 - A6</td>
<td>A1 - A2</td>
<td>A3 - A4</td>
</tr>
<tr>
<td>Light deformation</td>
<td>B5 - B6</td>
<td>B1 - B2</td>
<td>B3 - B4</td>
</tr>
<tr>
<td>Severe deformation</td>
<td>C5 - C6</td>
<td>C1 - C2</td>
<td>C3 - C4</td>
</tr>
</tbody>
</table>
### Effect of Extrusion on Surface Reactions

#### Table 8. Results of weighings.

<table>
<thead>
<tr>
<th>Weight of Soap (gm).</th>
<th>1.</th>
<th>2.</th>
<th>Av.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Not deformed</td>
<td>.0190</td>
<td>.0194</td>
<td>.0192</td>
</tr>
<tr>
<td>B. Light Deformation</td>
<td>.0163</td>
<td>.0155</td>
<td>.0159</td>
</tr>
<tr>
<td>C. Severe Deformation</td>
<td>.0219</td>
<td>.0159</td>
<td>.0189</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Weight Losses (ratio of weight loss to original coating weight is given in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. Pretreatment</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>A3 Stripped</td>
</tr>
<tr>
<td>A4</td>
</tr>
<tr>
<td>B3</td>
</tr>
<tr>
<td>B4</td>
</tr>
<tr>
<td>C3</td>
</tr>
<tr>
<td>C4</td>
</tr>
<tr>
<td>A1 Soap Removed</td>
</tr>
<tr>
<td>A2</td>
</tr>
<tr>
<td>B1</td>
</tr>
<tr>
<td>B2</td>
</tr>
<tr>
<td>C1 Soap Removed</td>
</tr>
<tr>
<td>C2</td>
</tr>
<tr>
<td>No.</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>A5</td>
</tr>
<tr>
<td>A6</td>
</tr>
<tr>
<td>A5</td>
</tr>
<tr>
<td>B6</td>
</tr>
<tr>
<td>B5</td>
</tr>
<tr>
<td>B6</td>
</tr>
</tbody>
</table>

Table 8 (Contd.)
Table 9. Variation in coating weight and depth of attack in various parts of extruded cups.

<table>
<thead>
<tr>
<th>No.</th>
<th>Area</th>
<th>Wt. of phosphate coating (mg/dm²)</th>
<th>Wt. of soap Coating (mg/dm²)</th>
<th>Depth of penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>G6 (Soap intact)</td>
</tr>
<tr>
<td>1</td>
<td>Rim</td>
<td>685</td>
<td>363</td>
<td>.076</td>
</tr>
<tr>
<td>2</td>
<td>O.D.upper</td>
<td>325</td>
<td>334</td>
<td>.036</td>
</tr>
<tr>
<td>3</td>
<td>O.D.middle</td>
<td>383</td>
<td>282</td>
<td>.020</td>
</tr>
<tr>
<td>4</td>
<td>O.D.lower</td>
<td>426</td>
<td>379</td>
<td>.033</td>
</tr>
<tr>
<td>5</td>
<td>Base</td>
<td>53</td>
<td>116</td>
<td>.020</td>
</tr>
<tr>
<td>6</td>
<td>I.D.</td>
<td>55</td>
<td>14</td>
<td>.006</td>
</tr>
</tbody>
</table>
Table 10. Standard Atmosphere Conditions employed in Experimental Furnace Treatments.

<table>
<thead>
<tr>
<th>Time Mins</th>
<th>Temperature</th>
<th>Pressure Torr</th>
<th>Flow 1/hr</th>
<th>Gas</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 15</td>
<td>Ambient</td>
<td>Evacuate to 0.1</td>
<td></td>
<td>Air</td>
<td>-</td>
</tr>
<tr>
<td>(2) 6</td>
<td>&quot;</td>
<td>Backfill to 760</td>
<td>30</td>
<td>N₂ or H₂</td>
<td>Only carried out if N₂ used in (2)</td>
</tr>
<tr>
<td>(3) 5</td>
<td>&quot;</td>
<td>Ambient</td>
<td>175</td>
<td>H₂</td>
<td></td>
</tr>
<tr>
<td>(4) 60</td>
<td>Heat to test temp.</td>
<td>&quot;</td>
<td>125</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>(5) 20</td>
<td>Soak</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>(6) 60</td>
<td>Sooil</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>(7) 8-10</td>
<td>Ambient</td>
<td>&quot;</td>
<td>30</td>
<td>N₂</td>
<td>Until flame disappeared.</td>
</tr>
</tbody>
</table>

Total Time 175 mins.

Volume of retort: 2.84 litres.
<table>
<thead>
<tr>
<th>Specification</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
</table>
| Size          | En 2E 61/64" Dia. | En 2E 1/2" Dia. | En 2E 23/8"x 1.104"
<p>| Form          | Hot rolled bar | Hot rolled bar | Bright rolled strip |
| C             | .135%      | .135%      | .125%      |
| Si            | .15%       | .17%       | .15%       |
| Mn            | .36%       | .35%       | .43%       |
| S             | .032%      | .030%      | .031%      |
| P             | .028%      | .035%      | .036%      |
| Ni            | .26%       | .26%       | .08%       |
| Cr            | .10%       | .10%       | .17%       |
| Mn            | .28%       | .38%       | .20%       |
| Mo            | -          | -          | .053%      |
| Hardness B.H.N. | 121      | 121        | 117        |
| Grain size (A.S.T.M. No.) | 5 | 5 | 6 - 7 |</p>
<table>
<thead>
<tr>
<th>Material</th>
<th>Grade</th>
<th>Specification and limits of important impurities. (Cpd. = Compound)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zine (metal)</td>
<td>A.R.</td>
<td>Iron (Fe) &lt; .005% Nitrogen opds. (N) &lt; .01%</td>
</tr>
<tr>
<td>Powder</td>
<td></td>
<td>Substances reducing KMnO₄ (0) &lt; .002%</td>
</tr>
<tr>
<td>Phosphoric OXIDE</td>
<td>A.R.</td>
<td>Assay: 98% min; Heavy Metals (Pb) &lt; .005%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td></td>
<td>Iron (Fe) &lt; .003%; Lower oxides (P₂O₅) &lt; .01%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sulphate (SO₄) &lt; .001%</td>
</tr>
<tr>
<td>Orthophosphoric</td>
<td>A.R.</td>
<td>Assay: 88% min; Alkalis &lt; 0.2%</td>
</tr>
<tr>
<td>Acid H₃PO₄</td>
<td></td>
<td>As &lt; .0001%; CL &lt; .0005%; Heavy Metals (Pb) &lt; .001%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe &lt; .001%; NO₃ &lt; .001%; Substances reducing KMnO₄ (0) &lt; .001%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SO₄ &lt; .002%</td>
</tr>
<tr>
<td>Sulphuric Acid H₂SO₄</td>
<td>A.R.</td>
<td>Assay: 98%; NH₃ &lt; .0003%; As &lt; .000007%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cl &lt; .00005%; Cu &lt; .0001%; Fe &lt; .05%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Free acid &lt; .05%; Pb &lt; .003%; Mn &lt; .05%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄ &lt; .002%; Zn &lt; .01%</td>
</tr>
<tr>
<td>Ferrous SULPHATE</td>
<td>A.R.</td>
<td>Assay: 99% min; Alkalis &lt; .08%; As &lt; .00004%;</td>
</tr>
<tr>
<td>FeSO₄. 7H₂O</td>
<td></td>
<td>Cl &lt; .00005%; Cu &lt; .0001%; Fe &lt; .05%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Free acid &lt; .05%; Pb &lt; .003%; Mn &lt; .05%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄ &lt; .002%; Zn &lt; .01%</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>A.R.</td>
<td>Assay 99% min. As &lt; .00002%; Ca, Mg, NH₃ &lt; .005%</td>
</tr>
<tr>
<td>Hydrated Na₂CO₃ 10H₂O</td>
<td></td>
<td>Cl &lt; .0015%; Pb &lt; .0005%; Fe &lt; .0003%; N &lt; .0005%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄ &lt; .0005%; K &lt; .01%; SIO₂ &lt; .002%; SO₄ &lt; .002%</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>A.R.</td>
<td>Assay 97% min; Na₂CO₃ &lt; 2%; Al &lt; .005%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NH₃ &lt; .001%; As &lt; .00007%; Cl &lt; .005%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb &lt; .001%; Fe &lt; .001%; NO₃ &lt; .002%;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄ &lt; .001%; SiO₂ &lt; .01%; SO₄ &lt; .003%</td>
</tr>
<tr>
<td>Iron Oxide (magnetic)</td>
<td>Precipitated</td>
<td>-</td>
</tr>
<tr>
<td>Material</td>
<td>Grade</td>
<td>Specification and limits of important impurities.</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------</td>
<td>---------------------------------------------------</td>
</tr>
<tr>
<td>Vanadium Pentoxide</td>
<td>Tech.</td>
<td>Assay 98.5% min.</td>
</tr>
<tr>
<td>$V_2O_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tri-Sodium Orthophosphate</td>
<td>A.R.</td>
<td>Assay 98% min; NaOH &lt; 1.5%; Cl &lt; 0.1%; SO$_4$ &lt; 0.05%</td>
</tr>
<tr>
<td>Na$_3$PO$_4$.12H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Orthovanadate</td>
<td>Tech.</td>
<td>$V_2O_5$ 22 - 25%, Ignition loss 45 - 58%; Cl &lt; 0.01%; SO$_4$ &lt; 0.01%</td>
</tr>
<tr>
<td>Na$_3$VO$_4$.14H$_2$O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>Specially fine</td>
<td>Assay 99% min. (gas liquid Chromatography) M.Pt. 70-71°C; Sulphated ash &lt; 0.05%</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>Synthetic</td>
<td>C 98 - 99%</td>
</tr>
</tbody>
</table>
Table 13. PROCESSING CONDITIONS FOR THE SURFACE TREATMENTS CARRIED OUT.

(a) Zinc Phosphate Treatment

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
<th>Strength</th>
<th>Temp.</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sodium Hydroxide Degrease</td>
<td>20% w/v</td>
<td>Boiling</td>
<td>10 min.</td>
</tr>
<tr>
<td>2.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 min.</td>
</tr>
<tr>
<td>3.</td>
<td>Sulphuric acid pickle</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Inhibitor Ferrolyte)</td>
<td>10% v/v</td>
<td>75°C</td>
<td>10 min.</td>
</tr>
<tr>
<td>4.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 min.</td>
</tr>
<tr>
<td>5.</td>
<td>Hot water rinse</td>
<td>-</td>
<td>70°C</td>
<td>2 min.</td>
</tr>
<tr>
<td>6.</td>
<td>Acidified Zinc Phosphate</td>
<td>Saturated</td>
<td>90°C</td>
<td>30 min.</td>
</tr>
<tr>
<td></td>
<td>(pH 4.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 min.</td>
</tr>
<tr>
<td>8.</td>
<td>Drying Oven</td>
<td>-</td>
<td>75°C</td>
<td>10 min.</td>
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<tr>
<td>9.</td>
<td>Measure coating weight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(selected samples)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Table 13 (Continued/...)

(b) Phosphoric Acid Treatment

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
<th>Strength</th>
<th>Temp.</th>
<th>Time</th>
</tr>
</thead>
</table>
| 1.  | Sodium Hydroxide Degrease         | 20% w/v | Boiling| 10 min.
| 2.  | Running water rinse                | -        | Cold   | 2 min. |
| 3.  | Sulphuric acid pickle             | 10% v/v  | 75°C   | 10 min.|
|     | (Inhibitor Ferrolyte)             |          |        |        |
| 4.  | Running water rinse                | -        | Cold   | 2 min. |
| 5.  | Hot water rinse                    | -        | 70°C   | 2 min. |
| 6.  | Orthophosphoric Acid 4M           | 392 ml/  | 90°C   | 15 min.|
|     | (Preliminary test conditions)     | litre    | 70°C   | 10 min.|
| 7.  | No rinse                          | -        | -      | -      |
| 8.  | Atmosphere dry on glass rods      |          |        |        |
Table 13 (Continued/...)

(c) Zinc Plating Treatment

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution</th>
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<th>Temp.</th>
<th>Time</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sodium hydroxide degrease</td>
<td>20% w/v</td>
<td>Boiling</td>
<td>10 min.</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Running water rinse</td>
<td></td>
<td>Cold</td>
<td>2 min.</td>
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</tr>
<tr>
<td>3.</td>
<td>Hydrochloric acid pickle</td>
<td>25% v/v</td>
<td>Cold</td>
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<tr>
<td>4.</td>
<td>Running water rinse</td>
<td></td>
<td>Cold</td>
<td>2 min.</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Second running water rinse</td>
<td></td>
<td>Cold</td>
<td>2 min.</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Sodium cyanide rinse</td>
<td>1½ oz/</td>
<td>Cold</td>
<td>1 min.</td>
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</tr>
<tr>
<td></td>
<td>gal.</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>7.</td>
<td>Running water rinse</td>
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<td>Cold</td>
<td>2 min.</td>
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<tr>
<td>8.</td>
<td>Zinc plate ZnO</td>
<td>7.5 oz/</td>
<td>24°C</td>
<td>30 min</td>
<td>30 amp/sq.ft</td>
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<tr>
<td></td>
<td>gal.</td>
<td></td>
<td></td>
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<td>NaCN</td>
<td>14.5</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>oz/gal</td>
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<td></td>
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<td>NaOH</td>
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<tr>
<td></td>
<td>oz/gal</td>
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<td>H₂MoO₄</td>
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<tr>
<td></td>
<td>oz/gal</td>
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<tr>
<td></td>
<td>Na₂S₂O₃</td>
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<tr>
<td></td>
<td>oz/gal</td>
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<td>Urea</td>
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Anodes: Zinc
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<th>Time</th>
<th>Current</th>
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<tr>
<td>9.</td>
<td>Running water rinse</td>
<td>-</td>
<td>Cold</td>
<td>2 min.</td>
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<tr>
<td>11.</td>
<td>Air blast dry</td>
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TABLE 14. RESULTS OF EXAMINATION OF THE COATINGS PRODUCED.

A. Coating wts. (mean of 3 results).

<table>
<thead>
<tr>
<th>Surface coating</th>
<th>Coating weight mg/dm²</th>
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<tbody>
<tr>
<td>Bonderite 181X (Lab. pilot plant)</td>
<td>179</td>
</tr>
<tr>
<td>Pure zinc phosphate</td>
<td>1070</td>
</tr>
<tr>
<td>Iron phosphate a) Original 70°C treatment</td>
<td>62</td>
</tr>
<tr>
<td>b) modified 90°C treatment</td>
<td>388</td>
</tr>
<tr>
<td>Bonderlube 235 (lab. pilot plant)</td>
<td>47</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>78</td>
</tr>
<tr>
<td>Graphite</td>
<td>102</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>37</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>11</td>
</tr>
<tr>
<td>Zinc</td>
<td>188</td>
</tr>
</tbody>
</table>

B. Chemical analysis of phosphate coatings.

<table>
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<tr>
<th></th>
<th>Zn%</th>
<th>Fe%</th>
<th>PO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Bonderite 181X - (Works Plant)</td>
<td>29.2</td>
<td>9.9</td>
<td>40.8</td>
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<tr>
<td>2. Bonderite 181X (Lab. Pilot Plant)</td>
<td>32.5</td>
<td>8.2</td>
<td>41.1</td>
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<tr>
<td>3. Pure Zinc Phosphate</td>
<td>34.8</td>
<td>6.6</td>
<td>42.6</td>
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<tr>
<td>4. Iron Phosphate (90°C treatment)</td>
<td>n.d.</td>
<td>37.0</td>
<td>42.2</td>
</tr>
<tr>
<td>Ref.</td>
<td>Test Piece Nos.</td>
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<td>Top Coat</td>
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<tr>
<td>------</td>
<td>----------------</td>
<td>-----------</td>
<td>----------</td>
</tr>
<tr>
<td>E1/a</td>
<td>C1,3,4</td>
<td>Bonderite 181X</td>
<td>Bonderlube 235</td>
</tr>
<tr>
<td></td>
<td>C7,9,10</td>
<td>Bonderite 181X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C13,15,16</td>
<td>Lab. Bonderite 181X</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C19,21,22</td>
<td></td>
<td>Lab. Bonderlube 235</td>
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<tr>
<td></td>
<td>C25,27,28</td>
<td>Iron Phosphate</td>
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</tr>
<tr>
<td></td>
<td>C31,33,34</td>
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<td>Bonderlube 235</td>
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<tr>
<td></td>
<td>C37,39,40</td>
<td>Zino Plate</td>
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</tr>
<tr>
<td></td>
<td>C43,45,46</td>
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<tr>
<td>E1/b</td>
<td>C2,5,6</td>
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<td>Bonderlube 235</td>
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<td>C8,11,12</td>
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<td>C14,17,18</td>
<td>Lab. Bonderite 181X</td>
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<td>C20,23,24</td>
<td></td>
<td>Lab. Bonderlube 235</td>
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<tr>
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<td>C26,29,30</td>
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<td></td>
<td>C32,35,36</td>
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<td>Bonderlube 235</td>
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<tr>
<td></td>
<td>C38,41,42</td>
<td>Zinc Plate</td>
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<td>------</td>
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<td>C44,47,48</td>
<td>Zino Plate</td>
<td>Bonderlube</td>
<td>Air</td>
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<tr>
<td>E4/a</td>
<td>P1 - 2</td>
<td>Zino Plate</td>
<td>Stearic Acid.</td>
</tr>
<tr>
<td>P11-12</td>
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<td>&quot;</td>
<td>Colloidal graphite</td>
</tr>
<tr>
<td>P21-22</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>E4/b</td>
<td>P3-4</td>
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<td>Stearic acid.</td>
</tr>
<tr>
<td>P13-14</td>
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<td>&quot;</td>
<td>Colloidal graphite</td>
</tr>
<tr>
<td>P23-24</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>E4/c</td>
<td>P5-6</td>
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<td>Stearic Acid.</td>
</tr>
<tr>
<td>P15-16</td>
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<tr>
<td>P25-26</td>
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<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>E4/d</td>
<td>P7-8</td>
<td>Zino Plate</td>
<td>Stearic Acid.</td>
</tr>
<tr>
<td>P17-18</td>
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<td>Colloidal graphite</td>
</tr>
<tr>
<td>P27-28</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>E4/e</td>
<td>P9-10</td>
<td>Zino Plate</td>
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<td>&quot;</td>
<td>Colloidal graphite</td>
</tr>
<tr>
<td>P29-30</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
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<td>Top Coat</td>
</tr>
<tr>
<td>------</td>
<td>----------------</td>
<td>-----------------</td>
<td>---------------</td>
</tr>
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<td>E4/f</td>
<td>P.105-106</td>
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<td>Stearic Acid.</td>
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<td>P.107-108</td>
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<tr>
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<td>P.109-110</td>
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</table>

### E.5 Influence of Sodium and moisture

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<th>Ref.</th>
<th>Test Piece Nos.</th>
<th>Undercoat</th>
<th>Top Coat</th>
<th>Atmosphere</th>
<th>Temperature</th>
<th>Time</th>
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</thead>
<tbody>
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<td>E5/a</td>
<td>P36-37</td>
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<td>Bonderlube</td>
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<td>Top Coat</td>
<td>Atmosphere</td>
<td>Temperature</td>
<td>Time</td>
</tr>
<tr>
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<td>Iron Phosphate</td>
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# Specimen bond with Ni-Cr wire.
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<th>Undercoat</th>
<th>Top Coat</th>
<th>Atmosphere</th>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.6. Effect of time on depth of diffused layer.</td>
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<td>P75-77</td>
<td>Iron Phosphate</td>
<td></td>
<td>NaOH \ Wet Hydrogen</td>
<td>1050°C</td>
<td>1 min</td>
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<td>P78-81</td>
<td>Iron Phosphate</td>
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<td>10 mins</td>
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<tr>
<td>P92-94</td>
<td>Zinc Phosphate</td>
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<td>30 mins</td>
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<td>P97-99</td>
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<td>Wet Hydrogen</td>
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<td>Zinc Phosphate</td>
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<td>E.6. Effect of heating in vacuum</td>
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<td>Bonderite 181X</td>
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<td>Bonderlube 235</td>
<td>10^{-1}Torr 650°C</td>
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<td>V1-3</td>
<td></td>
<td></td>
<td></td>
<td>10^{-6}Torr</td>
<td></td>
</tr>
<tr>
<td>V9-11</td>
<td>Bonderite 181X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V17-19</td>
<td>Bonderlube 235</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E6/c</td>
<td>P66-67</td>
<td>Bonderite</td>
<td></td>
<td></td>
<td>10^{-1}Torr 950°C</td>
<td>20 mins</td>
</tr>
<tr>
<td>P68-69</td>
<td>Bonderlube 235</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exp. No.</td>
<td>Test Piece No.</td>
<td>Undercoat</td>
<td>Top Coat</td>
<td>Atmosphere</td>
<td>Temperature</td>
<td>Time</td>
</tr>
<tr>
<td>---------</td>
<td>----------------</td>
<td>-----------</td>
<td>----------</td>
<td>------------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>66/d</td>
<td>V4 - 5</td>
<td></td>
<td></td>
<td>10^-6 Torr</td>
<td>950°C</td>
<td>20 mins</td>
</tr>
<tr>
<td></td>
<td>V12-13</td>
<td>Bonderite 181X</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>V20-21</td>
<td></td>
<td>Bonderlube 235</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>66/e</td>
<td>P61</td>
<td>Zinc Plate</td>
<td></td>
<td>10^-1 Torr</td>
<td>1050°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P70-71</td>
<td>Bonderite 181X</td>
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<td></td>
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<tr>
<td></td>
<td>P72-73</td>
<td>Bonderite 181X</td>
<td>Bonderlube 235</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>66/f</td>
<td>V6-8</td>
<td></td>
<td></td>
<td>10^-6 Torr</td>
<td>1050°C</td>
<td>20 mins</td>
</tr>
<tr>
<td></td>
<td>V14-16</td>
<td>Bonderite 181X</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>V22-24</td>
<td></td>
<td>Bonderlube 235</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67/a</td>
<td>S1 a</td>
<td>V_2O_5</td>
<td></td>
<td>Air</td>
<td>700°C</td>
<td>2 hrs</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>V_2O_5 + NaVO_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>P_2O_5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>P_2O_5 + NaPO_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67/b</td>
<td>S2a</td>
<td>V_2O_5</td>
<td></td>
<td>Wet H_2</td>
<td>1050°C</td>
<td>20 mins</td>
</tr>
<tr>
<td></td>
<td>b</td>
<td>V_2O_5 + NaVO_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>P_2O_5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>d</td>
<td>P_2O_5 + NaPO_3</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>---------------</td>
<td>--------------</td>
<td>-----------</td>
<td>----------</td>
<td>------------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>E10/a</td>
<td>S5-S10</td>
<td>Bonderite</td>
<td>Bonderlube</td>
<td>Test coupons for strip tests</td>
<td>not heat treated</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S11-S16</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>P111-112</td>
<td></td>
<td></td>
<td>Wet H₂</td>
<td>1050°C</td>
<td>20 mins</td>
</tr>
<tr>
<td></td>
<td>P113-114</td>
<td></td>
<td>Bonderlube</td>
<td></td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P115-116</td>
<td></td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td></td>
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<tr>
<td></td>
<td>P117-118</td>
<td></td>
<td>Bonderlube</td>
<td></td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(P111-114 NaOH Strip)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(P115-118 NaOH/NaCN Strip)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 16. RESULTS OF METALLOGRAPHIC MEASUREMENTS IN SERIES E.1.

Dimensions in mm. 181X = Bonderite 181X Proprietary Phosphate
                      235  = Bonderlube 235 Proprietary Lubricant.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Coating</th>
<th>Treatment</th>
<th>Depth of Pitting</th>
<th>Depth of Diffused Layer</th>
<th>Depth of Decarb. Inclusion Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, 1, 3, 4</td>
<td>181X/235</td>
<td>H₂ 950°C</td>
<td>.05/.12</td>
<td>.05/12</td>
<td>n.d.</td>
</tr>
<tr>
<td>C 7, 9, 10</td>
<td>181X</td>
<td></td>
<td>.02/.05</td>
<td>.08</td>
<td>n.d.</td>
</tr>
<tr>
<td>C 13, 15, 16</td>
<td>Lab 181X/235</td>
<td>H₂ 950°C</td>
<td>.02/.05</td>
<td>.05/.12</td>
<td>07/.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>15/.20</td>
</tr>
<tr>
<td>C 19, 21, 22</td>
<td>Lab 181X</td>
<td></td>
<td>.10</td>
<td>.05/.08</td>
<td>.01</td>
</tr>
<tr>
<td>C 25, 27, 28</td>
<td>Fe₃(PO₄)₂</td>
<td></td>
<td>.03/.05</td>
<td>.03/.15</td>
<td>.01</td>
</tr>
<tr>
<td>C 31, 33, 34</td>
<td>Fe₃(PO₄)₂ /235</td>
<td></td>
<td>.05</td>
<td>.16/.18</td>
<td>.05/.07</td>
</tr>
<tr>
<td>C 37, 39, 40</td>
<td>Zn</td>
<td></td>
<td>.02/.05</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>C 43, 45, 46</td>
<td>Zn/235</td>
<td></td>
<td>.02/.02</td>
<td>Nil</td>
<td>Nil</td>
</tr>
</tbody>
</table>

G.B.thickening Scale

| C 2, 5, 6 | 181X/235 | Air 950°C | .03/.04 | .10           |
| C 8, 11, 12| 181X     |           | .02/.04 | .05/.10       |
| C 14, 16, 17| Lab 181X/235 |       | .02/.03 | .10           |
| C 20, 23, 24| Lab 181X |           | .01/.03 | .10/.15       |
| C 26, 29, 30| Fe₃(PO₄)₂ |           | -       | .015          |
| C 32, 35, 36| Fe₃(PO₄)₂ /235 |       | -       | .02/.03       |
| C 38, 41, 42| Zn       |           | .02     | .16           |
| C 44, 47, 48| Zn/235  |           | .03     | .05/.15       |
## TABLE 17, RESULTS OF GRAVIMETRIC AND VISUAL EXAMINATION.

### Series E1.

**Dimensions in mm.**

**Wt. in gm.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wt. Change on anneal</th>
<th>Appearance after anneal</th>
<th>Wt. Change on Pickle</th>
<th>Appearance after pickle</th>
<th>Depth of pitting after pickle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1,3,4</td>
<td>-.0245</td>
<td>Clean</td>
<td>-.0627</td>
<td>Clean</td>
<td>.03/.08</td>
</tr>
<tr>
<td>C 7,9,10</td>
<td>-.0121</td>
<td>&quot;</td>
<td>-.0372</td>
<td>&quot;</td>
<td>.05/.10</td>
</tr>
<tr>
<td>C 13,15,16</td>
<td>-.0632</td>
<td>&quot;</td>
<td>-.1037</td>
<td>Smut</td>
<td>.05/.10</td>
</tr>
<tr>
<td>C 19,21,22</td>
<td>-.0614</td>
<td>&quot;</td>
<td>-.0717</td>
<td>Clean</td>
<td>.05/.07</td>
</tr>
<tr>
<td>C 25,27,28</td>
<td>-.4376</td>
<td>Sooty</td>
<td>-.2132</td>
<td>Black</td>
<td>.10</td>
</tr>
<tr>
<td>C 31,33,34</td>
<td>-.0483</td>
<td>Clean</td>
<td>-.1316</td>
<td>Black</td>
<td>.05/.10</td>
</tr>
<tr>
<td>C 37,39,40</td>
<td>-.0625</td>
<td>Green/Brown</td>
<td>-.0301</td>
<td>Clean</td>
<td>.07/.15</td>
</tr>
<tr>
<td>C 43,45,46</td>
<td>-.1481</td>
<td>&quot;</td>
<td>-.0610</td>
<td>Clean</td>
<td>.08/.11</td>
</tr>
<tr>
<td>C 2,5,6</td>
<td>+ .1587</td>
<td>Scale</td>
<td>-.1176</td>
<td>Residual Scale</td>
<td></td>
</tr>
<tr>
<td>C 8,11,12</td>
<td>+ .1546</td>
<td>&quot;</td>
<td>-.5601</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>C 14,16,17</td>
<td>+ .1127</td>
<td>&quot;</td>
<td>-.6543</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>C 20,23,24</td>
<td>+ .1438</td>
<td>&quot;</td>
<td>-.0668</td>
<td>Black</td>
<td></td>
</tr>
<tr>
<td>C 26,29,30</td>
<td>+ .4921</td>
<td>&quot;</td>
<td>-.0665</td>
<td>Black</td>
<td></td>
</tr>
<tr>
<td>C 32,35,36</td>
<td>+ .0652</td>
<td>&quot;</td>
<td>-.2205</td>
<td>Black</td>
<td></td>
</tr>
<tr>
<td>C 38,41,42</td>
<td>+ .1562</td>
<td>Loose White</td>
<td>-.5462</td>
<td>Green/Grey</td>
<td></td>
</tr>
<tr>
<td>C 44,47,48</td>
<td>-.0101</td>
<td>Deposit</td>
<td>-.4974</td>
<td>Green/Grey</td>
<td></td>
</tr>
</tbody>
</table>

* Flaking Scale.
TABLE 18. RESULTS OF METALLOGRAPHIC MEASUREMENTS IN
SERIES E.4.
Dimensions in mm.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Coating Treatment</th>
<th>Depth of Pitting</th>
<th>Depth of Diffused Layer</th>
<th>Depth of Inclusion Layer</th>
<th>Depth of Decarb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 1,2</td>
<td>Zn/Stearic</td>
<td>Exothermic</td>
<td>.03/.04</td>
<td>Nil.</td>
<td>.02</td>
</tr>
<tr>
<td>P 11,12</td>
<td>Zn/C</td>
<td></td>
<td>.01/.02</td>
<td></td>
<td>.04/.05</td>
</tr>
<tr>
<td>P 21,22</td>
<td>Zn</td>
<td></td>
<td>.01/.02</td>
<td></td>
<td>.02</td>
</tr>
<tr>
<td>P 3,4</td>
<td>Zn/Stearic</td>
<td>Air</td>
<td>.01/.04</td>
<td></td>
<td>.01/.04</td>
</tr>
<tr>
<td>P 13,14</td>
<td>Zn/C</td>
<td></td>
<td>.05</td>
<td></td>
<td>.05</td>
</tr>
<tr>
<td>P 23,24</td>
<td>Zn</td>
<td></td>
<td>.05</td>
<td></td>
<td>.05</td>
</tr>
<tr>
<td>P 5,6</td>
<td>Zn/Stearic</td>
<td>Air</td>
<td>.03/.04</td>
<td></td>
<td>.03/.04</td>
</tr>
<tr>
<td>P 15,16</td>
<td>Zn/C</td>
<td></td>
<td>.03/.05</td>
<td></td>
<td>.02</td>
</tr>
<tr>
<td>P 25,26</td>
<td>Zn</td>
<td></td>
<td>.01/.02</td>
<td></td>
<td>.02</td>
</tr>
<tr>
<td>P 7,8</td>
<td>Zn/Stearic</td>
<td>H2</td>
<td>.02</td>
<td></td>
<td>.02/.05</td>
</tr>
<tr>
<td>P 17,18</td>
<td>Zn/C</td>
<td></td>
<td>.05</td>
<td></td>
<td>.02</td>
</tr>
<tr>
<td>P 27,28</td>
<td>Zn</td>
<td></td>
<td>.05/.08</td>
<td></td>
<td>.05/.08</td>
</tr>
<tr>
<td>P 9,10</td>
<td>Zn/Stearic</td>
<td>H2</td>
<td>n-d</td>
<td>n-d</td>
<td>n-d</td>
</tr>
<tr>
<td>P 19,20</td>
<td>Zn/C</td>
<td></td>
<td>n-d</td>
<td>n-d</td>
<td>n-d</td>
</tr>
<tr>
<td>P 29,30</td>
<td>Zn</td>
<td></td>
<td>n-d</td>
<td>n-d</td>
<td>n-d</td>
</tr>
<tr>
<td>P 105,106</td>
<td>Fe₃(PO₄)₂ /Stearic</td>
<td></td>
<td></td>
<td>.03/.08</td>
<td>.01</td>
</tr>
<tr>
<td>P 107,108</td>
<td>Fe₃(PO₄)₂ /C</td>
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<td>.04/.08</td>
<td>.01</td>
</tr>
<tr>
<td>P 109,110</td>
<td>Fe₃(PO₄)₂ /C</td>
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<td></td>
<td>.05/.07</td>
<td>.01</td>
</tr>
<tr>
<td>P 33x,34y</td>
<td>Zn</td>
<td>Dry H₂</td>
<td>.03</td>
<td>Nil.</td>
<td>.03</td>
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</tbody>
</table>

* Exothermic gas - a complex reducing gas produced by partly burned town gas.
TABLE 19. RESULTS OF GRAVIMETRIC AND VISUAL EXAMINATION.

SERIES E. 4.

Dimensions in mm.  wts. in gm.

<table>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1, 2</td>
<td>- .0930</td>
<td>Clean Matte</td>
<td>- .0343</td>
<td>Clean</td>
<td>.05/.07</td>
</tr>
<tr>
<td>P11, 12</td>
<td>- .0852</td>
<td>&quot;</td>
<td>- .0601</td>
<td>&quot;</td>
<td>.08/.09</td>
</tr>
<tr>
<td>P21, 22</td>
<td>- .0742</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P3, 4</td>
<td>- .0588 x</td>
<td>Scale</td>
<td>- .0431</td>
<td>&quot;</td>
<td>.06/.07</td>
</tr>
<tr>
<td>P13, 14</td>
<td>- .0682 x</td>
<td>&quot;</td>
<td>- .0471</td>
<td>&quot;</td>
<td>.07/.09</td>
</tr>
<tr>
<td>P23, 24</td>
<td>- .0588 x</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P5, 6</td>
<td>- .1730</td>
<td>&quot;</td>
<td>- .0353</td>
<td>&quot;</td>
<td>.04/.06</td>
</tr>
<tr>
<td>P15, 16</td>
<td>- .0409</td>
<td>&quot;</td>
<td>- .0320</td>
<td>&quot;</td>
<td>.07/.08</td>
</tr>
<tr>
<td>P25, 26</td>
<td>- .0471</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P 7, 8</td>
<td>- .1786</td>
<td>Bright</td>
<td>- .0529</td>
<td>&quot;</td>
<td>.06/.08</td>
</tr>
<tr>
<td>P 17, 18</td>
<td>- .0751</td>
<td>Grey Matte</td>
<td>- .0467</td>
<td>&quot;</td>
<td>.04/.06</td>
</tr>
<tr>
<td>P 27, 28</td>
<td>- .0817</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P 9, 10</td>
<td>- .0715</td>
<td>Bright</td>
<td>- .0436</td>
<td>&quot;</td>
<td>.05</td>
</tr>
<tr>
<td>P 19, 20</td>
<td>- .0543</td>
<td>&quot;</td>
<td>- .0443</td>
<td>&quot;</td>
<td>.04/.05</td>
</tr>
<tr>
<td>P 29, 30</td>
<td>- .0877</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P 105, 106</td>
<td>- .0540</td>
<td>Clean resolidified</td>
<td>- .1577</td>
<td>Black</td>
<td>.05/.10</td>
</tr>
<tr>
<td>P 107, 108</td>
<td>- .0507</td>
<td>&quot;</td>
<td>- .1390</td>
<td>&quot;</td>
<td>.07/.15</td>
</tr>
<tr>
<td>P 109, 110</td>
<td>- .0626</td>
<td>&quot;</td>
<td>- .1610</td>
<td>&quot;</td>
<td>.07/.12</td>
</tr>
</tbody>
</table>

x Flaking Scale.
| Sample No. | Coating | Treatment | Depth of Pitting | Depth of Diffused Layer | Depth of Inclusion Layer | Depth of Decarb/
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P 36.37</td>
<td>181X/235</td>
<td>Dry H₂</td>
<td>-</td>
<td>.03/.08</td>
<td>-</td>
<td>.20/.30</td>
</tr>
<tr>
<td>P 40.41</td>
<td>Zn/235</td>
<td>&quot;</td>
<td>-</td>
<td>N11</td>
<td>.02/.03</td>
<td>.20/.30</td>
</tr>
<tr>
<td>P 44.45</td>
<td>181X/NaOH</td>
<td>&quot;</td>
<td>-</td>
<td>.04/.05</td>
<td>.01/.02</td>
<td>.20</td>
</tr>
<tr>
<td>P 48.49</td>
<td>Zn/NaOH</td>
<td>&quot;</td>
<td>.08</td>
<td>N11</td>
<td>-</td>
<td>.25</td>
</tr>
<tr>
<td>P 52.53</td>
<td>Fe₃(PO₄)₂</td>
<td>&quot;</td>
<td>-</td>
<td>.05/.08</td>
<td>-</td>
<td>.20</td>
</tr>
<tr>
<td>P 56.57</td>
<td>NaOH</td>
<td>&quot;</td>
<td>.02</td>
<td>N11</td>
<td>-</td>
<td>.30</td>
</tr>
<tr>
<td>P 38.39</td>
<td>181X/235</td>
<td>Wet H₂</td>
<td>-</td>
<td>.15</td>
<td>.05/.10</td>
<td>.40/.45</td>
</tr>
<tr>
<td>P 42.43</td>
<td>Zn/235</td>
<td>&quot;</td>
<td>-</td>
<td>N11</td>
<td>.03</td>
<td>.40</td>
</tr>
<tr>
<td>P 46.47</td>
<td>181X/NaOH</td>
<td>&quot;</td>
<td>-</td>
<td>.18</td>
<td>.02/.07</td>
<td>.35</td>
</tr>
<tr>
<td>P 50.51</td>
<td>Zn/NaOH</td>
<td>&quot;</td>
<td>.08</td>
<td>N11</td>
<td>-</td>
<td>.30</td>
</tr>
<tr>
<td>P 54.55</td>
<td>Fe₃(PO₄)₂</td>
<td>&quot;</td>
<td>-</td>
<td>.07/.08</td>
<td>.07</td>
<td>.30</td>
</tr>
<tr>
<td>P 58.59</td>
<td>NaOH</td>
<td>&quot;</td>
<td>.10</td>
<td>N11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C51, 52</td>
<td>Fe₃(PO₄)₂</td>
<td>&quot;</td>
<td>-</td>
<td>.16</td>
<td>.08</td>
<td>.35</td>
</tr>
</tbody>
</table>

TABLE 20. RESULTS OF METALLOGRAPHIC MEASUREMENTS IN SERIES E.5.

181X = Bonderite 181X Proprietary Phosphate.
235 = Bonderlube 235 Proprietary Lubricant.

Dimensions in mm.
TABLE 21. RESULTS OF GRAVIMETRIC AND VISUAL EXAMINATION.
SERIES E 5.

Wts. in gm.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Appearance after anneal</th>
<th>Wt. change on pickle</th>
<th>Ratio to original coating Wt.</th>
<th>Appearance after pickle</th>
</tr>
</thead>
<tbody>
<tr>
<td>P36,37</td>
<td>Resolidified</td>
<td>-0.0675</td>
<td>1.33</td>
<td>Black</td>
</tr>
<tr>
<td>P40,41</td>
<td>Bright</td>
<td>-0.0136</td>
<td>0.27</td>
<td>Clean</td>
</tr>
<tr>
<td>P44,45</td>
<td>Resolidified</td>
<td>-0.0623</td>
<td>1.23</td>
<td>Black</td>
</tr>
<tr>
<td>P48,49</td>
<td>Bright</td>
<td>-0.0088</td>
<td>0.17</td>
<td>Clean</td>
</tr>
<tr>
<td>P52,53</td>
<td>Pitted/resolidified</td>
<td>-0.0790</td>
<td>1.56</td>
<td>Black</td>
</tr>
<tr>
<td>P56,57</td>
<td>Pitted</td>
<td>-0.0098</td>
<td>0.19</td>
<td>Clean</td>
</tr>
<tr>
<td>P38,39</td>
<td>Grey/Resolidified</td>
<td>-0.0131</td>
<td>0.26</td>
<td>Black</td>
</tr>
<tr>
<td>P42,43</td>
<td>Brown</td>
<td>-0.0147</td>
<td>0.29</td>
<td>Clean</td>
</tr>
<tr>
<td>P46,47</td>
<td>Resolidified</td>
<td>-0.0125</td>
<td>0.25</td>
<td>Black</td>
</tr>
<tr>
<td>P50,51</td>
<td>Dark Patches</td>
<td>-0.0080</td>
<td>0.16</td>
<td>Clean</td>
</tr>
<tr>
<td>P54,55</td>
<td>Dark/Resolidified</td>
<td>-0.0133</td>
<td>0.26</td>
<td>Black</td>
</tr>
<tr>
<td>P58,59</td>
<td>Pitted</td>
<td>-0.0131</td>
<td>0.26</td>
<td>Clean</td>
</tr>
</tbody>
</table>
### TABLE 22. RESULTS OF METALLOGRAPHIC MEASUREMENTS IN SERIES E.8.

**Dimensions in mm.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Coating Treatment</th>
<th>Depth of Pitting</th>
<th>Depth of Diffused Layer</th>
<th>Depth of Inclusion Layer</th>
<th>Depth of Decarb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 88</td>
<td>Fe₃(PO₄)₂</td>
<td>None</td>
<td>0.02/.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P 75</td>
<td></td>
<td>NaOH</td>
<td>0.02/.03</td>
<td>0.053</td>
<td>0.032</td>
</tr>
<tr>
<td>P 75</td>
<td>1 min.</td>
<td>1050°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 81</td>
<td>10 min.</td>
<td>1050°C</td>
<td>0.01/.02</td>
<td>0.088</td>
<td>0.038</td>
</tr>
<tr>
<td>P 82</td>
<td>30 min.</td>
<td>1050°C</td>
<td>0.05</td>
<td>0.097</td>
<td>0.053</td>
</tr>
<tr>
<td>P 87</td>
<td>90 min.</td>
<td>1050°C</td>
<td>0.05</td>
<td>0.174</td>
<td>0.072</td>
</tr>
<tr>
<td>P 96</td>
<td>(Zn,Fe)₃(PO₄)₂</td>
<td>None</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P 96</td>
<td>NaOH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P 89</td>
<td></td>
<td>1 min.</td>
<td>1050°C</td>
<td>0.02/.03</td>
<td>0.073</td>
</tr>
<tr>
<td>P 93</td>
<td></td>
<td>10 min.</td>
<td>1050°C</td>
<td>-</td>
<td>0.123</td>
</tr>
<tr>
<td>P 99</td>
<td></td>
<td>30 min.</td>
<td>1050°C</td>
<td>-</td>
<td>0.120</td>
</tr>
<tr>
<td>P 100</td>
<td></td>
<td>90 min.</td>
<td>1050°C</td>
<td>-</td>
<td>0,200</td>
</tr>
</tbody>
</table>
## TABLE 23. RESULTS OF GRAVIMETRIC AND VISUAL EXAMINATION

**Series E.8.**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Appearance after Anneal</th>
<th>Wt. loss after 1st Pickle (15 min)</th>
<th>Appearance after 1st Pickle</th>
<th>Wt. loss after 2nd Pickle (60 min.)</th>
<th>Appearance after 2nd Pickle</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 75</td>
<td>Loose ash</td>
<td>0.162</td>
<td>Black Smut</td>
<td>1.689</td>
<td>Clean/ Pitted</td>
</tr>
<tr>
<td>P 81</td>
<td>Bright/ash</td>
<td>0.177</td>
<td>&quot;</td>
<td>1.482</td>
<td>&quot;</td>
</tr>
<tr>
<td>P 82</td>
<td>Resolidified</td>
<td>0.184</td>
<td>&quot;</td>
<td>1.191</td>
<td>&quot;</td>
</tr>
<tr>
<td>P 87</td>
<td>Resolidified</td>
<td>0.139</td>
<td>&quot;</td>
<td>0.907</td>
<td>&quot;</td>
</tr>
<tr>
<td>P 89</td>
<td>Loose Ash</td>
<td>0.089</td>
<td>&quot;</td>
<td>2.265</td>
<td>&quot;</td>
</tr>
<tr>
<td>P 93</td>
<td>Resolidified</td>
<td>0.178</td>
<td>&quot;</td>
<td>2.271</td>
<td>&quot;</td>
</tr>
<tr>
<td>P 99</td>
<td>Resolidified</td>
<td>0.138</td>
<td>&quot;</td>
<td>2.606</td>
<td>&quot;</td>
</tr>
<tr>
<td>P 100</td>
<td>Resolidified</td>
<td>0.129</td>
<td>&quot;</td>
<td>1.205</td>
<td>&quot;</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Coating</td>
<td>Treatment</td>
<td>Depth of Pitting</td>
<td>Depth of Diffused Layer</td>
<td>Depth of Inclusion Layer</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>--------------------</td>
<td>------------------</td>
<td>-------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>V1</td>
<td>None</td>
<td>Vac $10^{-5}$</td>
<td>.02</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>P63</td>
<td>181X</td>
<td>Vac $10^{-1}$</td>
<td>.05/.10</td>
<td>.07</td>
<td>.05</td>
</tr>
<tr>
<td>V9</td>
<td></td>
<td>Vac $10^{-5}$</td>
<td>tr.</td>
<td>.02</td>
<td>—</td>
</tr>
<tr>
<td>P64</td>
<td>181X/</td>
<td>Vac $10^{-1}$</td>
<td>.03/.05</td>
<td>tr.</td>
<td>.02</td>
</tr>
<tr>
<td>235</td>
<td></td>
<td>235</td>
<td>.05</td>
<td>.1</td>
<td>.10</td>
</tr>
<tr>
<td>V17</td>
<td></td>
<td>Vac $10^{-5}$</td>
<td>.04/.06</td>
<td>tr.</td>
<td>.02</td>
</tr>
<tr>
<td>V4</td>
<td>None</td>
<td>Vac $10^{-5}$</td>
<td>.03</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>P66</td>
<td>181X</td>
<td>Vac $10^{-1}$</td>
<td>.05</td>
<td>.07</td>
<td>.05</td>
</tr>
<tr>
<td>V12</td>
<td>181X</td>
<td>Vac $10^{-5}$</td>
<td>.01/.02</td>
<td>.01</td>
<td>.02/.07</td>
</tr>
<tr>
<td>P69</td>
<td>181X/</td>
<td>Vac $10^{-1}$</td>
<td>.05</td>
<td>.12</td>
<td>.05/.10</td>
</tr>
<tr>
<td>235</td>
<td>235</td>
<td>235</td>
<td>.05</td>
<td>.05</td>
<td>.65</td>
</tr>
<tr>
<td>V20</td>
<td>181X/</td>
<td>Vac $10^{-5}$</td>
<td>—</td>
<td>.02/.03</td>
<td>.02/.05</td>
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<td>235</td>
<td>235</td>
<td>235</td>
<td>.05</td>
<td>.02/.06</td>
<td>.02/.06</td>
</tr>
<tr>
<td>V6</td>
<td>None</td>
<td>Vac $10^{-5}$</td>
<td>.04</td>
<td>Nil</td>
<td>.02</td>
</tr>
<tr>
<td>P70</td>
<td>181X</td>
<td>Vac $10^{-1}$</td>
<td>.05</td>
<td>.02/.06</td>
<td>.02/.06</td>
</tr>
<tr>
<td>V14</td>
<td>181X</td>
<td>Vac $10^{-5}$</td>
<td>.10/.15</td>
<td>tr.</td>
<td>.10/.15</td>
</tr>
<tr>
<td>P72</td>
<td>181X/</td>
<td>Vac $10^{-1}$</td>
<td>.05</td>
<td>.05</td>
<td>—</td>
</tr>
<tr>
<td>235</td>
<td>235</td>
<td>235</td>
<td>.05</td>
<td>.05</td>
<td>—</td>
</tr>
<tr>
<td>Sample No</td>
<td>Coating</td>
<td>Treatment</td>
<td>Depth of Pitting</td>
<td>Depth of Diffused Layer</td>
<td>Depth of Inclusion Layer</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>-----------</td>
<td>------------------</td>
<td>------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>V22</td>
<td>181X/235</td>
<td>Vao $10^{-5}$ 1050°C</td>
<td>.02</td>
<td>.01</td>
<td>-</td>
</tr>
<tr>
<td>P61</td>
<td>Zn</td>
<td>Vao $10^{-1}$ 1050°C</td>
<td>.05/.07</td>
<td>Nil</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE 25. RESULTS OF VISUAL EXAMINATION
SERIES E.6.

Appearance after heating.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Crystalline Coating</th>
<th>Bright Needles</th>
<th>Loose Flakes</th>
<th>Bright Globules and Exudations</th>
<th>&quot;Resolidified&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>V1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P63</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V9</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P64</td>
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<tr>
<td>V17</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>V4</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>P66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V12</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P69</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V20</td>
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</tr>
<tr>
<td>V6</td>
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<td>V14</td>
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<tr>
<td>P72</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>V22</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P61</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 26:

Weight losses on pickling samples with different reaction coatings.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Wt. loss after 15 min. pickle (gm.)</th>
<th>Wt. loss after 75 min. pickle (actual) gm.</th>
<th>Wt. loss after 75 min. pickle (adjusted) gm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.77</td>
<td>0.162</td>
<td>1.451</td>
<td>1.689</td>
</tr>
<tr>
<td>78</td>
<td>0.177</td>
<td>1.286</td>
<td>1.482</td>
</tr>
<tr>
<td>84</td>
<td>0.184</td>
<td>1.191</td>
<td>1.191</td>
</tr>
<tr>
<td>85</td>
<td>0.139</td>
<td>0.782</td>
<td>0.907</td>
</tr>
<tr>
<td>91</td>
<td>0.089</td>
<td>1.923</td>
<td>2.265</td>
</tr>
<tr>
<td>94</td>
<td>0.178</td>
<td>2.033</td>
<td>2.271</td>
</tr>
<tr>
<td>98</td>
<td>0.138</td>
<td>2.606</td>
<td>2.606</td>
</tr>
<tr>
<td>101</td>
<td>0.129</td>
<td>1.111</td>
<td>1.205</td>
</tr>
</tbody>
</table>

* Adjusted to take account of portion removed for metallographic examination after first pickle. Weight loss multiplied by weight before removal of section/weight after removal of section.
### TABLE 27. TENSILE TEST RESULTS.

Key to abbreviations used to indicate the pretreatment:
- **B** = Phosphated (Bonderite 181X)
- **Zn** = Phosphated (Zinc-Iron Phosphate)
- **F** = Phosphated (Iron Phosphate)
- **L** = Lubricated (Bonderlube 235)
- **Na** = Coated with Na₂CO₃

**Ni Cr** = Bonded with Nickel Chromium wire

**950 (1050)** = Annealed for 20 mins at 950°C (1050°C)

**P** = Pickled.

T1 - T12 are round specimens 0.564" dia. x 2" gauge length

T13 - T24 are flat specimens 1.00" x .520" x 2" gauge length

<table>
<thead>
<tr>
<th>No.</th>
<th>Y.P.(t.s.i)</th>
<th>M.S.</th>
<th>True.U.T.S.</th>
<th>El%</th>
<th>R.A.%</th>
<th>Surface Tears</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper</td>
<td>Lower</td>
<td>(t.s.i)</td>
<td>(t.s.i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T1</td>
<td>B - Ni Cr - 950</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.4</td>
<td>13.6</td>
<td>21.8</td>
<td>53.3</td>
<td>51</td>
<td>74</td>
<td>Yes</td>
</tr>
<tr>
<td>T2</td>
<td>B - 950 - P - B-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>14.0</td>
<td>22.0</td>
<td>56.0</td>
<td>49</td>
<td>75</td>
<td>Yes</td>
</tr>
<tr>
<td>T3</td>
<td>B - 950 - P - B-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.0</td>
<td>13.6</td>
<td>22.0</td>
<td>53.8</td>
<td>50</td>
<td>74</td>
<td>Yes</td>
</tr>
<tr>
<td>T4</td>
<td>B - L - NiCr - 950</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.6</td>
<td>13.2</td>
<td>21.6</td>
<td>55.5</td>
<td>48</td>
<td>75</td>
<td>Yes</td>
</tr>
<tr>
<td>T5</td>
<td>B - L - 950 - P-B-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.2</td>
<td>13.8</td>
<td>22.1</td>
<td>53.8</td>
<td>49</td>
<td>74</td>
<td>Yes</td>
</tr>
<tr>
<td>T6</td>
<td>B - L - 950 - P-B-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.4</td>
<td>13.7</td>
<td>21.8</td>
<td>54.4</td>
<td>49</td>
<td>75</td>
<td>Yes</td>
</tr>
<tr>
<td>T7</td>
<td>Ni Cr-950 - P-B-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.5</td>
<td>14.4</td>
<td>21.8</td>
<td>56.7</td>
<td>49</td>
<td>76</td>
<td>No</td>
</tr>
<tr>
<td>T8</td>
<td>950 - P-B-L</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>18.0</td>
<td>13.4</td>
<td>22.0</td>
<td>53.1</td>
<td>47</td>
<td>74</td>
<td>No</td>
</tr>
<tr>
<td>T9</td>
<td>250 - P-B-L</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.2</td>
<td>13.7</td>
<td>22.1</td>
<td>51.9</td>
<td>50</td>
<td>73</td>
<td>No</td>
</tr>
<tr>
<td>No.</td>
<td>Y.P. (t.s.i.)</td>
<td>M.S. (t.s.i.)</td>
<td>True U.T.S. (t.s.i.)</td>
<td>El %</td>
<td>R.A. %</td>
<td>Surface Tears</td>
</tr>
<tr>
<td>-----</td>
<td>---------------</td>
<td>---------------</td>
<td>----------------------</td>
<td>------</td>
<td>--------</td>
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</tr>
<tr>
<td></td>
<td>Upper</td>
<td>Lower</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T10</td>
<td>250</td>
<td>17.5</td>
<td>14.2</td>
<td>22.4</td>
<td>54.9</td>
<td>50</td>
</tr>
<tr>
<td>T11</td>
<td>250</td>
<td>17.6</td>
<td>13.9</td>
<td>21.8</td>
<td>52.8</td>
<td>55</td>
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<tr>
<td>T12</td>
<td>Ni Cr - 950</td>
<td>17.1</td>
<td>13.7</td>
<td>21.9</td>
<td>54.9</td>
<td>49</td>
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<td>2nd Series</td>
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<td></td>
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<tr>
<td>T13</td>
<td>Zn - 1050</td>
<td>15.7</td>
<td></td>
<td>23.8</td>
<td>41.1</td>
<td>32</td>
</tr>
<tr>
<td>T14</td>
<td>Zn - 1050 - P</td>
<td>15.4</td>
<td>15.0</td>
<td>23.2</td>
<td>42.4</td>
<td>30</td>
</tr>
<tr>
<td>T15</td>
<td>Zn - Na - 1050</td>
<td>15.0</td>
<td>14.9</td>
<td>23.0</td>
<td>43.1</td>
<td>30</td>
</tr>
<tr>
<td>T16</td>
<td>Zn - Na - 1050 - P</td>
<td>15.7</td>
<td>14.5</td>
<td>23.3</td>
<td>41.4</td>
<td>34</td>
</tr>
<tr>
<td>T17</td>
<td>Fe - 1050</td>
<td>15.4</td>
<td></td>
<td>23.5</td>
<td>33.0</td>
<td>28</td>
</tr>
<tr>
<td>T18</td>
<td>Fe - 1050 - P</td>
<td>15.4</td>
<td>14.8</td>
<td>23.1</td>
<td>35.3</td>
<td>29</td>
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<tr>
<td>T19</td>
<td>Fe - Na - 1050</td>
<td>15.3</td>
<td>14.3</td>
<td>22.3</td>
<td>40.4</td>
<td>28</td>
</tr>
<tr>
<td>T20</td>
<td>Fe - Na - 1050 - P</td>
<td>15.9</td>
<td></td>
<td>22.8</td>
<td>39.2</td>
<td>27</td>
</tr>
<tr>
<td>T21</td>
<td>Fe - Ni Cr - 1050</td>
<td>15.0</td>
<td>14.8</td>
<td>24.4</td>
<td>26.8</td>
<td>24</td>
</tr>
<tr>
<td>T22</td>
<td>Fe - Na - Ni Cr - 1050</td>
<td>16.1</td>
<td>14.6</td>
<td>22.9</td>
<td>39.5</td>
<td>32</td>
</tr>
<tr>
<td>T23</td>
<td>None</td>
<td>15.7</td>
<td>14.9</td>
<td>23.9</td>
<td>49.6</td>
<td>37</td>
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<tr>
<td>T24</td>
<td>None</td>
<td>14.4</td>
<td></td>
<td>23.1</td>
<td>53.5</td>
<td>42</td>
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## Table 28. Surface hardness of Test Specimens.

Treatment Code as for Table 27.

<table>
<thead>
<tr>
<th>No.</th>
<th>Treatment</th>
<th>Surface hardness (H.V. 2°/2 Kg)</th>
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<tbody>
<tr>
<td>13</td>
<td>Zn – 1050</td>
<td>247</td>
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<tr>
<td>14</td>
<td>Zn – 1050 - P</td>
<td>123</td>
</tr>
<tr>
<td>15</td>
<td>Zn – Na – 1050</td>
<td>224</td>
</tr>
<tr>
<td>16</td>
<td>Zn – Na – 1050 - P</td>
<td>97</td>
</tr>
<tr>
<td>16</td>
<td>Fe – 1050</td>
<td>186</td>
</tr>
<tr>
<td>18</td>
<td>Fe – 1050 - P</td>
<td>181</td>
</tr>
<tr>
<td>19</td>
<td>Fe – Na – 1050</td>
<td>93</td>
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<tr>
<td>20</td>
<td>Fe – Na – 1050 - P</td>
<td>96</td>
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<tr>
<td>21</td>
<td>Fe – Ni Cr – 1050</td>
<td>201</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>445 (at wire mark)</td>
</tr>
<tr>
<td>22</td>
<td>Fe – Na – Ni Cr – 1050</td>
<td>127</td>
</tr>
<tr>
<td>23</td>
<td>1050</td>
<td>107</td>
</tr>
<tr>
<td>24</td>
<td>None</td>
<td>137</td>
</tr>
</tbody>
</table>
Table 29. ANALYSIS OF DIFFUSED SURFACE LAYER

Treatment: 20 min at 1050°C in hydrogen

Depth of diffused layer: .08 - .12 mm

(a) Zinc

<table>
<thead>
<tr>
<th>Coating</th>
<th>% Zn</th>
<th>Wt. absorbed on .2 mm deep layer</th>
<th>Total Zn available in coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>.010</td>
<td>1.6</td>
<td>0</td>
</tr>
<tr>
<td>Bonderite 181X (Works Plant)</td>
<td>.008</td>
<td>1.3</td>
<td>94.8</td>
</tr>
<tr>
<td>Bonderite 181X (Lab. Plant)</td>
<td>.011</td>
<td>1.7</td>
<td>58.2</td>
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<tr>
<td>Zinc Iron Phosphate</td>
<td>.013</td>
<td>2.1</td>
<td>372.5</td>
</tr>
<tr>
<td>Iron Phosphate</td>
<td>.007</td>
<td>1.1</td>
<td>0</td>
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</table>

(b) Phosphorus

<table>
<thead>
<tr>
<th>Coating</th>
<th>% P</th>
<th>% P increase over core</th>
<th>Wt. absorbed on .2 mm deep layer</th>
<th>Total P available in coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>.029</td>
<td>.001</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Bonderite 181X (Works Plant)</td>
<td>.065</td>
<td>.037</td>
<td>5.9</td>
<td>25.4</td>
</tr>
<tr>
<td>Bonderite 181X (Lab. Plant)</td>
<td>.063</td>
<td>.035</td>
<td>5.5</td>
<td>13.9</td>
</tr>
<tr>
<td>Zinc-Iron Phosphate</td>
<td>.116</td>
<td>.088</td>
<td>14.1</td>
<td>86.8</td>
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<tr>
<td>Iron Phosphate</td>
<td>.073</td>
<td>.045</td>
<td>7.1</td>
<td>31.1</td>
</tr>
<tr>
<td>Zinc Iron Phosphate</td>
<td>.16</td>
<td>.132</td>
<td>20.9</td>
<td>86.8</td>
</tr>
</tbody>
</table>

(measured by Electron Microscope)
(c) Qualitative X-ray and Fluorescence Analysis

1. P not detectable (Atomic number below 20)
2. Zn - no significant increase
3. Cr and Ni - significantly higher in areas in contact with Ni - Cr alloys
TABLE 30. EFFECTIVENESS OF STRIPPING SOLUTIONS
Specimen Area = 20 cm²

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimens coated with commercial phosphate and lubricant.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 5</td>
<td>.0572</td>
<td>.0196</td>
<td>- .0420</td>
<td></td>
<td>.0102</td>
</tr>
<tr>
<td>S 6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.0134</td>
</tr>
<tr>
<td>S 7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 8</td>
<td>.0594</td>
<td>.0211</td>
<td></td>
<td>.0792</td>
<td>.0001</td>
</tr>
<tr>
<td>S 9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Wt. Mg Pyrophosphate after ignition gm.</td>
</tr>
<tr>
<td>S 10</td>
<td></td>
<td></td>
<td></td>
<td>.0776</td>
<td>.0001</td>
</tr>
<tr>
<td>Specimens coated with commercial phosphate only.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 11</td>
<td>.0585</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 12</td>
<td>-</td>
<td>-</td>
<td>- .0310</td>
<td></td>
<td>.0080</td>
</tr>
<tr>
<td>S 13</td>
<td>-</td>
<td>-</td>
<td>- .0289</td>
<td></td>
<td>.0125</td>
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<tr>
<td>S 14</td>
<td>.0612</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S 15</td>
<td>-</td>
<td>-</td>
<td>- .0592</td>
<td></td>
<td>.0001</td>
</tr>
<tr>
<td>S 16</td>
<td>-</td>
<td>-</td>
<td>- .0622</td>
<td></td>
<td>.00015</td>
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</table>

175
<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating</th>
<th>Stripping Solution</th>
<th>Wt. loss on pickle after annealing (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 111</td>
<td>Bonderite 181X</td>
<td>20% NaOH</td>
<td>0.0626</td>
</tr>
<tr>
<td>P 113</td>
<td>Bonderite 181X + Bonderlube 235</td>
<td></td>
<td>0.0937</td>
</tr>
<tr>
<td>P 115</td>
<td>Bonderite 181X + NaOH/NaCN</td>
<td></td>
<td>0.0004</td>
</tr>
<tr>
<td>P 117</td>
<td>Bonderite 181X + Bonderlube 235</td>
<td></td>
<td>0.0004</td>
</tr>
</tbody>
</table>
Figure 1: Critical Strain Grain Growth in a 0.08% C Steel. Preformed Specimen Subcritically Annealed. 2 Hours at 650°C. x 100

Etchant 3% Nital
Figure 2: Stages in the Manufacture of the Extruded Component.

Scale: Full Size.
Figure 3: Typical Extrusion Crack.
A: Regression Line, Base Thickness on Cracking.
B: Regression Line, Cracking on Base Thickness.

Correlation Coefficient: -0.462

Figure 4: Correlation Between Cracking Severity and Base Thickness.
A: Regression Line, Slug Weight on Cracking.
B: Regression Line, Cracking on Slug Weight.

Correlation Coefficient: -0.472

Figure 5: Correlation Between Cracking Severity and Preform Slug Weight.
A: Regression Line, Cracking on Coating Weight.

B: Regression Line, Coating Weight on Cracking.

Correlation Coefficient: +0.617

Figure 6: Correlation Between Cracking Severity and Coating Weight.
A: Regression Line, Cracking on Hardness.
B: Regression Line, Hardness on Cracking.
Correlation Coefficient: +0.160

Figure 7: Correlation Between Cracking Severity and Hardness at Lip of Cup.
A: Regression Line, Slug Weight on Coating Weight.
B: Regression Line, Coating Weight on Slug Weight.
Correlation Coefficient: -0.832

Figure 8: Correlation Between Preform Slug Weight and Coating Weight.
Direction of Metal Flow  Direction of Puheh

Figure 9: Inner Surface of Satisfactory Cup. x2

Figure 10: Inner Surface of Unsatisfactory Cup. x2
Figure 11: Surface of underweight slug of high coating weight after stripping, showing rough surface. $x4$.

Figure 12: Surface of slug of normal weight and coating weight after stripping. $x4$. 
Figure 13: A series of cracks at an early stage of development. \( \times 100 \) Etchant 3% Nital
Direction of extrusion

Figure 14: A fully developed circumferential crack and associated disturbance of grain flow. \( \times 50 \) Etchant 3% Nital
Direction of extrusion
Figure 15: A Comparison of Changes in Coating Weight after Annealing and Pickling, with Different Stripping Pretreatments.
Figure 16: Surface of preformed slug normalised in reducing atmosphere without stripping, showing scars from reaction with furnace belt. x4

Figure 17: Surface of a similar slug showing blisters in the surface layer. x30
Figure 18: Section through one of the Blisters shown in figure 17.

Etchant 3% Nital x 300
Figure 19: Surface of a slug after stripping, normalising in a reducing atmosphere, and pickling. x4

Figure 20: Surface of a slug normalised in a reducing atmosphere without stripping, and pickling. x4
Figure 21: Section through a slug normalised in a reducing atmosphere without stripping, and pickled, showing alloying with mesh belt. 
Etchant 3% Nital x300

Figure 22: Section through a similar slug to that in figure 21, showing sub-surface attack. 
Etchant 3% Nital x300
Figure 23: Section through O.D. of sample A0 (cropped slug, phosphated, lubricated and annealed at 950 °C in a reducing atmosphere without deformation). Etchant 3% Nital x300

Figure 24: Section through cropped edge of sample A2 (treated as sample A0, out with lubricant omitted). Etchant 3% Nital x300
Figure 25: Relationship Between Coating Weight Before Annealing and Depth of Penetration, in Different Areas of Extruded Cups.
Figure 27: Heating and Cooling Curves for Components in the Retort Furnace at 650°C, 950°C and 1050°C.
Survey Taken after Two Hours at Temperature, Thermocouple Imbedded in Component. (Fig. 27)

Figure 28: Temperature Distribution within Retort at 650°C, 950°C and 1050°C.
Type (a) Test Piece.

Type (b) Test Piece.

Type (c) Test Piece.

Type (d) Test Piece.

Figure 29: Types of Test Piece Employed in the Investigation.
Figure 30: General view of the retort furnace.
Figure 51: General view of the high vacuum furnace.
Figure 52: Specimen 033, coated with a light iron phosphate coating (0.2 mg/m²), plus Bonderlube 235, after heating for 20 minutes at 950°C in hydrogen.

Etchant 3% Nital x 200
Figure 33: Specimen C39, zinc plated and heated to 950°C for 20 minutes in hydrogen, x 300

Etchant 3% Nital

Figure 34: Specimen C45, zinc plated and coated with Bonderlube 235, after heating to 950°C for 20 minutes in hydrogen.

Etchant 3% Nital x 300
Figure 35: Specimen C47, zinc plated and coated with Bonderlube 235, after heating to 950°C for 20 minutes in air.

Etchant 3% Nital  x 300

Figure 36: Specimen P42, zinc plated and coated with Bonderlube 235, after heating to 1020°C for 20 minutes in wet hydrogen.

Etchant Stead's reagent  x 300
Figure 37: Specimen P100, coated with zinc phosphate and sodium hydroxide, and heated for 90 minutes at 1020° C in hydrogen.

Etchant 3% Nital × 200

Figure 38: Specimen P37, coated with iron phosphate and sodium hydroxide, and heated for 90 minutes at 1020° C in hydrogen.

Etchant 3% Nital × 200
Figure 39: Cambridge X-ray Scanning Microanalyser, Specimen P.99.
Zinc Radiation.
Upper Line: Slow Scan across Diffused Layer.
Lower Line: Zn Zero Level.

Horizontal Axis: 1 division = 0.02 mm.
Figure 40: Specimen 15B, coated with Bonderite 101X and Bonderlupe 235, after heating in air to 1050°C for a short time. The white substance is zinc oxide.  x 2

Figure 41: Specimen 01, coated with Bonderite 101X and Bonderlupe 235, after heating at 950°C for 20 minutes in hydrogen. Etchant Stead's reagent  x 100
Figure 42: Specimen P52, coated with iron phosphate and sodium hydroxide after heating to 1050°C for 20 minutes in dry hydrogen. Etchant Stead's reagent x 300

Figure 43: Specimen S2/o (steel plate) coated with phosphorus pentoxide powder, after heating to 1050°C for 20 minutes in wet hydrogen. x 300
Figure 44: Cambridge X-ray Scanning Microanalyser, Specimen P.99.

Line 1: Slow Scan across Diffused layer, P radiation.
Line 2: P Zero Level.
Line 3: Slow Scan across Diffused Layer, Mn radiation.

Horizontal Axis: 1 division = 0.02 mm.
Figure 4b: Surface of sample P2b, coated with Bonderite 101X and Bonderite 227, after heating to 1020°C for 20 minutes in hydrogen. x 2

Figure 4c: Sample P2b, coated with Bonderite 101X and Bonderite 227, after heating to 1050°C for 20 minutes in dry hydrogen. Etchant Stead's reagent x 200
Figure 40: Sample P62, coated with iron phosphate and sodium hydroxide, after heating at 1050°C for 20 minutes in hydrogen. 
Etchant Stead's reagent x 200

Figure 40: Sample P50, coated with sodium hydroxide only, after heating at 1050°C for 20 minutes in hydrogen. 
Etchant Stead's reagent x 200
Figure 49: Sample S2/a, impression filled with 71% P₂O₅ and 29% NaPO₃, heated to 1020°C for 20 minutes in hydrogen. x 1

Figure 50: The same sample at higher magnification, showing the dendritic pattern in impression. x 20
Figure 21: Section through the upper part of impression S2/a, showing the phosphide eutectic. x 200

Figure 22: Section through the base of impression S2/a, showing the subsurface inclusions. x 200
Figure 33: Specimen Tz0, coated with iron phosphate and sodium carbonate after heating at 1050°C for 10 minutes in wet hydrogen. x 2

Figure 34: Specimen Tz0 after a further 10 minutes at 1050°C in wet hydrogen. x 2
Figure 22: Specimen TzO, after pickling for 15 minutes in inhibited sulphuric acid. x 2
Figure 57: Sample P36, coated with Bonderite 151X and Bonderlube 235, after heating to 1050°C in wet hydrogen. x300
Etchant Stead's Reagent

Figure 59: Sample P54, coated with iron phosphate and sodium hydroxide, after heating to 1050°C in wet hydrogen. x300 Etchant Stead's Reagent
Figure 60: Sample C17, coated with Bonderite 181X and Bonderlube 235, after heating to 950°C in air. x 300

Etchant: 3% Nital

Figure 61: Sample C35, coated with iron phosphate and Bonderlube 235, after heating to 950°C in air. x 300

Etchant: 3% Nital
Sample Po0, not heated.

Sample P15, heated 1 minute.

Sample Po1, heated 10 minutes.

Sample Po2, heated 30 minutes.

Figure 62: The effect of time on samples coated with iron phosphate and sodium hydroxide and heated to 1050°C in hydrogen.

Etchant Stead's reagent × 300
Sample P96, not heated.

Sample P99, heated 1 minute.

Sample P99, heated 10 minutes.

Sample P100, heated 90 minutes.

Figure 63: The effect of time on samples coated with zinc phosphate and sodium hydroxide and heated to 1050°C in hydrogen.

Etchant Sted's reagent x 200
Figure 64: The Effect of Annealing Time on Depth of Diffusion Effects with Two Types of Coating.
Figure 65: The Effect of Annealing Time at 1050°C on Weight Loss on Subsequent Pickling for 15 Minutes in Inhibited H₂SO₄.
Figure 66: The Effect of Annealing Time at 1050°C on Weight Loss on Subsequent Pickling for 75 Minutes in Inhibited H₂SO₄.
Figure 67: Sample P85, coated with iron phosphate and sodium hydroxide, heated at 1050°C for 90 minutes in hydrogen, pickled for 15 minutes in inhibited 10% sulphuric acid. x 300

Etchant Stea's reagent.

Figure 68: Sample P85 after pickling for a further 60 minutes.

Etchant Stea's reagent x 300
Figure 09: Sample P91a, coated with zinc phosphate and sodium hydroxide, heated at 1050°C for 1 minute in hydrogen, pickled for 75 minutes in inhibited sulphuric acid.

Etchant Stead's reagent  x 500

Figure 10: Sample P95a, coated with zinc phosphate and sodium hydroxide, heated at 1050°C for 30 minutes in hydrogen, pickled for 75 minutes in inhibited sulphuric acid.

Etchant Stead's reagent  x 200
Figure 71: Sample P101a, another part of the surface.
Etchant Stead's reagent  x200

Figure 71: Sample P101a, coated with zinc phosphate and sodium hydroxide, heated at 1020°C for 90 minutes in inhibited sulphuric acid.
Etchant Stead's reagent  x200
Figure 73: Specimen T2), not coated, after heating at 1050°C in hydrogen and tensile testing. \( x \beta \)

Figure 74: Specimen T1), coated with zinc phosphate, after heating at 1050°C in hydrogen and tensile testing. \( x \beta \)
Figure 75: Specimen T21, coated with iron phosphate and bound with Nichrome wire, after heating at 1050°C for 20 minutes in hydrogen and tensile testing. x 6

Figure 76: Specimen T18, coated with iron phosphate, after heating at 1050°C for 20 minutes in hydrogen, pickling, and tensile testing. x 6
Figure 77: Specimen S2a, coated with vanadium pentoxide, after heating at 1050°C for 20 minutes in wet hydrogen. x 300
Etchant 3% Nital

Figure 78: Specimen S2/c, coated with 79% vanadium pentoxide and 21% sodium vanadate, after heating at 1050°C for 20 minutes in wet hydrogen. x 300
Etchant 3% Nital
Figure 79: Graphical Summary of the Results Obtained by X-ray Analysis of Coating Residues.
**Figure 60:** Electron probe microphotograph, showing the distribution of iron in specimen P99. The edge of the specimen is at the top, brightness is proportional to iron concentration, the dark areas being slag. For optical microstructure see figure 63. x 300 (enlarged 1.5 times in reproduction.)

**Figure 61:** Electron probe microphotograph showing the distribution of phosphorus in specimen P99. Particulars as for figure 60.
Figure 62: electron probe photomicrograph showing the distribution of manganese in specimen P99. Details are as given in figure 50. Arrow indicates position of the slow line scans given in figures 39 and 44.
Figure S3: Sample P72, coated with Bonderite 181X and Bonderlube 235, after heating to 1050°C for 20 minutes in a low vacuum (10⁻¹ Torr).

Etchant Stead's reagent  x 300
Figure 04: Sample Pl14, coated with Bonderite 161x and Bonderlube 235, stripped in 20% sodium hydroxide, and annealed at 1050°C in hydrogen.

Etchant 3% Nital x 300

Figure 05: Sample Pl16, treated as Pl14 (figure 04) except that it was stripped in sodium hydroxide-sodium cyanide solution before heat treatment.

Etchant 3% Nital x 300